

**INFRARED ANALYSIS APPLIED TO  
CLAY MINERALS**

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INFRARED ANALYSIS APPLIED TO CLAY MINERALS

by

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Adviser

Rensselaer Polytechnic Institute

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## FOREWORD

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Appreciation is also expressed to Assistant Professor J. E. MUNZER for his many valuable suggestions and advice given throughout the execution of this study, and to Associate Professor S. V. BEST and Assistant Professor W. KELLEHER for their recommendations and advice.

The complete cooperation of the Department of Chemistry, particularly Professor S. E. WIBERLY, for the use of infrared equipment is deeply appreciated. Thanks is also expressed to Professor S. MACKAY of the Department of Metallurgical Engineering for his aid in construction of the sample preparation die.



## ABSTRACT

The application of infrared analysis to the field of clay mineralogy is investigated using the relatively new double beam type spectrophotometer principle and the potassium bromide pellet technique for preparing sample cells.

A brief history of infrared spectroscopy is presented, pointed particularly to the clay field, with only three investigations of significance being found in the literature.

The theory of infrared absorption is discussed along with theoretical applications of the technique. The lattice structures of the three major clay minerals are described.

Procedures developed for preparing sample and KBr mixtures by hand and with a small dental type amalgamator and the results using the two methods are discussed. Variables including sample quantity, particle size, window pressing pressure, and time duration of pressure application are investigated.

Twenty four reference clay minerals collected and identified by the American Petroleum Institute are analyzed by the infrared process and the resulting spectra then compared with the results of the API investigators. A close correlation of absorption band center positions is evident.

Investigations of a preliminary nature are performed to determine the effects of high temperature, saturation with organic ions, saturation with inorganic ions, and mixtures of clay minerals on the infrared spectra. Results that are reasonable in the light of known facts are observed in all instances with the exception of the effect of saturating





the clays with inorganic ions. In this case the results are inconclusive.

Identification of clay minerals present in three natural clay samples is performed with results that indicate that the infrared technique will prove to be a useful addition to clay mineral investigative methods.

Recommendations concerning an alternative design for a window die which was suggested by the results of the investigation are included along with construction details for local fabrication of the die.



PART I.  
INTRODUCTION

A. Historical Review

Although application of infrared analysis to the field of clay mineralogy dates back less than a decade, its use in other fields, particularly that of organic chemistry began in the early part of the century. Infrared radiation was discovered by William Herschel<sup>17\*</sup> in 1800 at which time he constructed the first infrared spectrophotometer consisting of three thermometers and a prism to measure the temperature of refracted sunlight. In 1835 Ampere<sup>2</sup> and Herschel's son theorized that visible and infrared radiation differed only in the degree of their refraction by prisms. In 1880 Langley developed a bolometer and galvanometer arrangement to permit the use of diffraction gratings for the dispersion of the spectrum, making possible the accurate determination of wave length.

Experimental evidence of a relationship between molecular structure and characteristic absorption frequencies was published in 1905<sup>8</sup>. Following World War I, there occurred a rapid growth in the use of infrared analysis in chemistry. In the middle 30's the first industrial applications were developed. Commercial spectrophotometers began to appear in 1940 as infrared analysis in industry proved highly successful. In 1944, Barnes<sup>3</sup> and his associates summarized the status of the field at that time, including in their publication a reference spectra library of organic compounds and an extensive bibliography.

\*Subscript numbers refer to similarly numbered items in PART VII, LITERATURE CITED.



Infrared absorption in clay mineralogy has thus far been only superficially explored. Keller and Pickett<sup>19, 20</sup> presented two papers in 1949 which included sample spectra for some of the more common clay minerals. This work was followed quickly by the American Petroleum Institute report on reference clay minerals<sup>1</sup> which included a section on infrared analysis. Absorption spectra were included as obtained by different investigators at different laboratories using slightly varied techniques on identical series of clay mineral samples.

Modern infrared instrumentation, including a detailed description of the instrument used for this study, is described in the works of Liston,<sup>21, 22, 23</sup> Harley,<sup>14</sup> and Williams.<sup>27</sup>

#### B. Statement of Problem

No published works of significance have appeared on the application of infrared to clay minerals since 1950. Infrared spectra included in the API report<sup>1</sup> which were obtained from similar samples by different investigators possess the same general characteristics but show wide variation in detail. Further investigation is necessary to show whether or not these minor variations have significance or are merely the results of difference in instrumentation and testing techniques. "The causes of many absorption bands shown by the clay minerals are not yet understood. For example, the causes of variations in the spectra within the montmorillonite group cannot yet be related to variations of composition or structure."<sup>10</sup>

Subsequent to the performance of the studies reported in 1950, many improvements have been made in the sensitivity and response charac-



teristics of infrared detectors. Improvements have also been made in source stability and recording mechanisms. Combining these improvements with the development of the potassium bromide pellet technique for handling solid samples, it is believed that it is now possible to determine the cause of minor variations described above. Such is the primary objective of the study reported herein.





## PART II.

## THEORY

A. Origin of Infrared Spectra

Infrared radiation makes up only a small portion of the electromagnetic spectrum. Its relative position in the electromagnetic spectrum is shown in Figure I. Within very approximate limits the infrared band is divided into the following subdivisions: the Rotational Region from 350 microns to 250 microns, the Fundamental Vibration Region from 25 microns to 2.5 microns, the Overtone Region from 2.5 microns to 1.3 microns, and the Photographic Region from 1.3 microns to 0.75 microns. Of primary interest to the clay mineral field is the Fundamental Vibration Region.

The atoms of any molecule at a temperature above that of absolute zero are continually moving about their equilibrium positions. The amplitude of these oscillations is extremely small ( $10^{-9}$  to  $10^{-10}$  centimeters). The frequency of oscillation is quite high ( $10^{13}$  to  $10^{14}$  cycles per second) and of the same order as those of infrared radiation. Molecular vibrations accompanied by a change in dipole moment resulting from the atomic motion are referred to as infrared active. Infrared active vibrations will absorb by resonance all or a portion of such infrared radiation as is incident upon the molecule when the radiation frequency equals that of the intramolecular vibrations. A sample of like molecules that is exposed to a series of successive monochromatic bands of infrared will show a plot of percent radiation transmitted versus wave length of frequency that can be interpreted in terms of intramolecular motion. Any vibrational energy that is absorbed will set up an instantaneous dipole



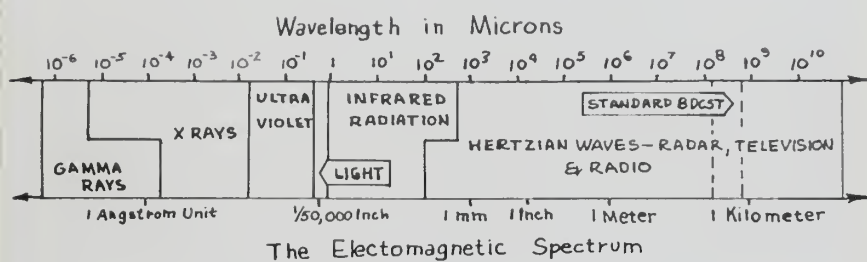


Figure I. The Electromagnetic Spectrum.



moment in the molecules and an absorption band will result. These bands are characteristic for different linkages and bonds in a molecule and to some extent are an indication of the size and structure of the molecule. Characteristic vibrations not associated with a dipole moment will not absorb in the infrared and consequently no absorption bands will result.

### B. Characteristics of Vibrations

Vibrations of one atom with respect to another occur with two types of motion. A "stretching" motion occurs when atoms move along the axis while a "bending" motion will produce angular deformation of the interatomic bond.

Several vibratory motions are likely to appear in a given atomic structure. Such seemingly complicated motions can be shown to be merely summations of a number of simple oscillations. Such oscillations are referred to as normal or fundamental modes of vibration. A fundamental mode is said to exist when the center of gravity of the molecule remains fixed and all the atoms in the molecule move in the same phase and frequency of vibration.

A linear molecule of  $n$  atoms can be shown by mathematics to possess  $3n-5$  fundamental modes while a nonlinear molecule possesses  $3n-6$  such modes. Each fundamental mode will occur without affecting the others except in instances when the symmetry of the molecule results in any of the modes becoming degenerate or equivalent. In such a case a lesser number of fundamental modes will appear to exist than is computed by the formula.

The frequency of vibration of an atomic arrangement will depend upon the individual masses of the atoms involved and the restoring force



between the atoms. By an approximation utilizing Hooke's Law, Barnes<sup>3</sup> illustrates this with the equation

$$\nu = \frac{1}{2c\pi} \sqrt{\frac{k}{u}}$$

in which  $\nu$  is the vibration frequency in reciprocal centimeters,

$c$  is the velocity of light,

$u$  is the reduced mass of the vibrating atoms, and

$k$  is the force constant which exists between atoms.

By substitution of numerical values for constants the equation reduces to

$$\nu = 1307 \sqrt{\frac{k}{u}} \quad \text{cm.}^{-1}$$

is  $k$  is used as a pure number and  $u$  is in dimensionless atomic mass units.

Using known values of  $k$  and  $u$ , the C-H bond frequency in methane would equal:

$$\nu = 1307 \sqrt{\frac{5}{1}} = 2920 \text{ cm.}^{-1}$$

Similarly C=O in acetone equals  $1730 \text{ cm.}^{-1}$  and C≡H in HCN is 2000. A check of the infrared spectra of these compounds gives strong absorption bands at 2915, 1744, and 2089  $\text{cm.}^{-1}$  "The slight variations observed in these frequency positions of maximum absorption for molecules that are closely related chemically...makes it possible to use the exact frequency empirically as a means not only of telling that a given atomic group is present but also of determining the relation of this group to the remainder of the molecule. Conversely, once the value of the absorption frequency of a given band has been determined experimentally, it is often possible to calculate the force constant,  $k$ , or the binding energy between the vibrating atoms."<sup>3</sup>





From the above calculations it might naturally be concluded that the possibility exists that all fundamental modes of vibration could be determined mathematically. Providing the strengths of all of the interatomic forces are known, this is true at least theoretically; however, such calculations depend upon the number of atoms in a molecule and their geometrical symmetry. Water with just three atoms has been subjected to thorough mathematical analysis but involves only a third degree equation. Where a geometrical symmetry has been destroyed the situation is changed as, for example, in the case of ortho-chlorophenol, where "a rigorous treatment would require the solution of a thirty-third degree equation."<sup>3</sup>

### C. Theoretical Applications

Infrared spectroscopy has both qualitative and quantitative applications. Qualitatively, the process is useful in the identification of compounds; recognition of specific chemical bonds, linkages, or groups; determination of gross structural features; and the qualitative analysis of a mixture of several compounds. Quantitatively, the infrared technique is useful in measurement of reaction rates, the determination of thermodynamic data, and process analysis and control.

Certain advantages over other analytical processes are evident in the field of infrared. Providing reasonable care is taken in preparation, storage, and handling of samples, they may be used repeatedly over long periods of time with no changes in their characteristics. Where time is important infrared tests can be performed quickly -- survey runs of samples can be performed in as little as five minutes of time. Such a run is often all that is required to place a clay mineral in one of the



three general classifications. The chief value of infrared analysis lies in the fact that the infrared absorption spectrum of a compound is a unique physical characteristic of that compound which cannot be duplicated by any other compound. The specific values of both the frequency and intensity of the absorption bands of the spectra will serve to positively identify the compound since the complete spectral matching of a known and an unknown sample is considered adequate proof of the identity of an unknown.

#### D. The Clay Minerals

The term "clay" is used to denote a type of rock and also to denote particle size. As a rock term "clay implies a natural earthy, fine-grained material which develops plasticity when mixed with a limited amount of water."<sup>10</sup> As a particle size term, clay is usually considered in soil investigations to be that fraction smaller than 4 microns in size. Neither of the above concepts provide a complete or accurate definition which will suit all requirements. For the purpose of this paper, clay will be defined as a disperse system of the colloidal products of weathering in which secondary minerals smaller than two microns predominate.

The clay minerals are essential constituents of all clays and largely determine a clay's properties. Clay minerals may be generally classes as hydrous aluminum silicates and have been proved by X-rays to be distinctly crystalline minerals. Following the initial generalizations of Pauling<sup>26</sup> numerous investigators have agreed basically on the structure of the three classes of clay minerals as described herein.



Structural Units. Two structural units are involved in the atomic lattices of the clay minerals. One unit consists of two sheets of closely spaced hydroxal groups or oxygen atoms which are held together by aluminum (most common), magnesium or iron atoms in such a way that each aluminum, magnesium or iron atom is surrounded by six hydroxals or oxygen atoms, three from each sheet. A sketch of the Al-OH octahedral unit cell is shown in Figure II along with the sheet structure.

The other unit consists of silica tetrahedrons of four oxygen atoms (or hydroxals if needed to balance the structure) equidistant from the central silica atom as shown in Figure III.

Kaolinites. The structure of kaolinite as postulated by Gruner,<sup>12</sup> Grim,<sup>11</sup> and Pauling<sup>26</sup> is shown in Figure IV. Kaolinite consists essentially of a 1:1 lattice structure composed of a single silica tetrahedral sheet combined in a unit with an alumina octahedral sheet in such a manner that the tips of the silica sheet and one layer of the alumina sheet form a common layer. In the common layer, two-thirds of the atoms are shared by the silica and aluminum with oxygen atoms replacing the hydroxals. The charges within the crystalline structure are balanced. The sheets are continuous in the a and b directions and are stacked one above the other in the c direction. A strong bond exists between the adjoining O and OH atoms of the stacked unit cells and as a consequence the clay is relatively stable and low in exchange capacity.

The theoretical chemical composition is  $\text{SiO}_2$ -46.54%,  $\text{Al}_2\text{O}_3$  39.5% and  $\text{H}_2\text{O}$ -13.96%. In the API report<sup>1</sup> quantitative analyses of natural kaolinites show the composition to vary as follows:

$\text{SiO}_2$       44.82 - 54.17%





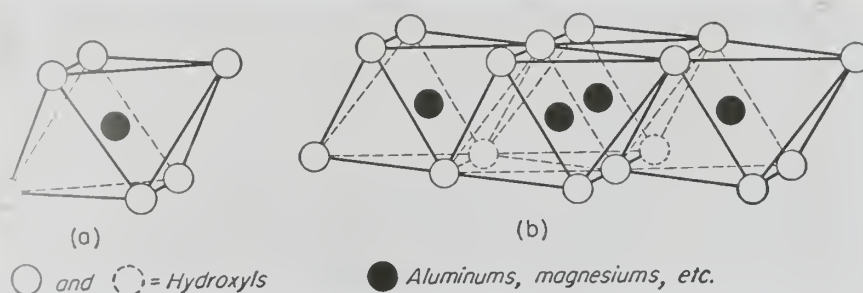


Figure II. The Alumina Octahedral and Sheet Structure. After Grim.

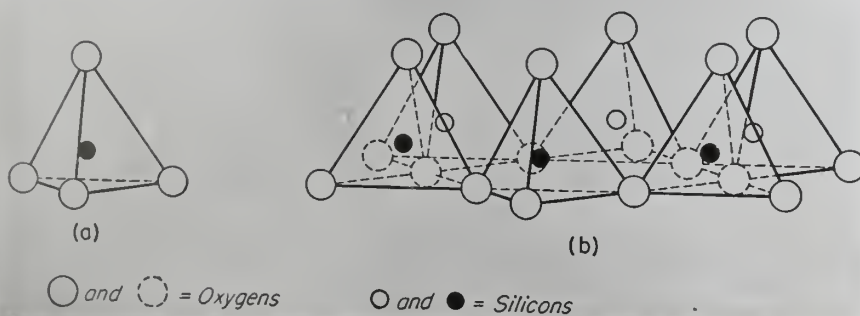


Figure III. The Silica Tetrahedral and Sheet Structure. After Grim.





$\text{Al}_2\text{O}_3$  29.36 - 38.89%

$\text{H}_2\text{O}$  10.05 - 14.14%

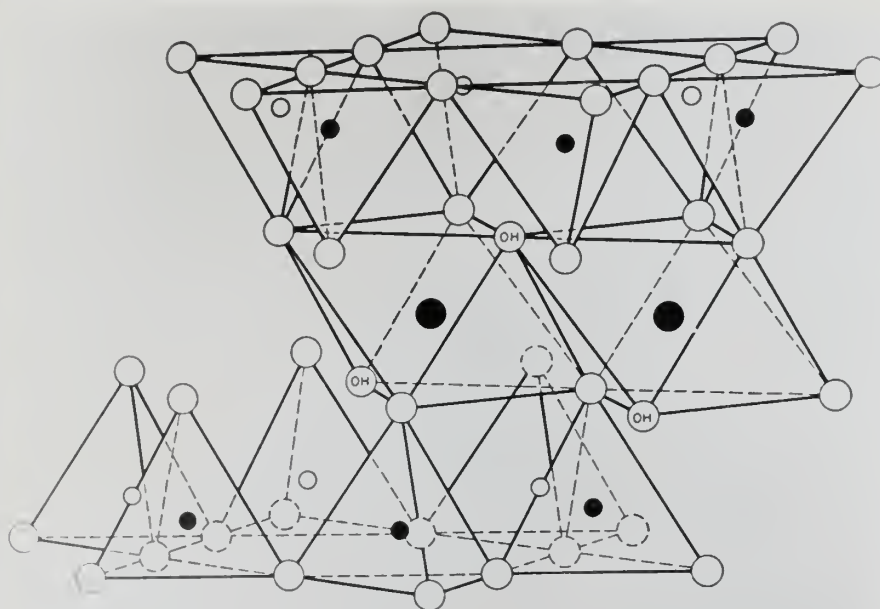
Most of the natural kaolinites possess fractional percentages of some or all of the following oxides:  $\text{FeO}$ ,  $\text{MgO}$ ,  $\text{CaO}$ ,  $\text{Na}_2\text{O}$ ,  $\text{TiO}_2$ ,  $\text{K}_2\text{O}$ ,  $\text{Fe}_2\text{O}_3$ , and  $\text{MnO}$ . The clay minerals halloysite, dickite, nacrite, and anauxite are included in the kaolinite classification.

Montmorillonites. Because of the extremely small size of the montmorillonite particles, accurate determination of the structure has been difficult. The most accepted structure as suggested by Hoffman and later modified by Marshall,<sup>24</sup> Hendricks,<sup>16</sup> and Grim<sup>11</sup> is shown in Figure V. Montmorillonite is considered to possess a 2:1 crystal lattice structure consisting of two silica tetrahedral sheets surrounding a central alumina octahedral sheet. As in the kaolinite structure, the atoms common to both the tetrahedral and octahedral layers become O replacing OH. The sheets are continuous in the a and b directions and are stacked one above the other in the c direction; however, in the stacking of the montmorillonite in silica-alumina-silica units the oxygen atoms of the outer edges of the silica sheets are adjacent to those of the next unit cell. A weak bond consequently exists between the lattices along with excellent cleavage and relative instability. Montmorillonites are notorious for their swelling characteristics and their high exchange capacity.

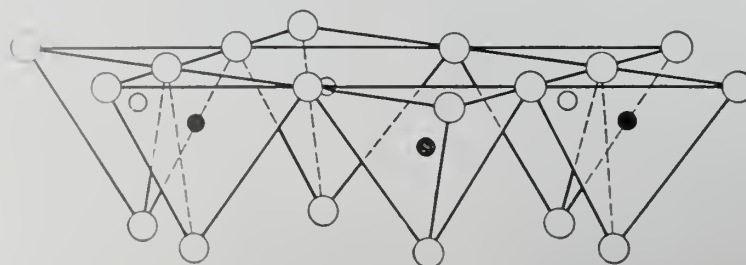
The theoretical chemical composition, ignoring the interlayer material which may or may not be present, is  $\text{SiO}_2$  - 66.7%,  $\text{Al}_2\text{O}_3$  - 28.3%, and water 5%. In the API report<sup>1</sup> quantitative analyses of natural montmorillonites show the following composition variations:

$\text{SiO}_2$  47.64 - 60.96%





*Exchangeable Cations*  
 $n\text{H}_2\text{O}$



○ *Oxygens*    (OH) *Hydroxyls*    ● *Aluminum, iron, magnesium*  
 ○ and ● *Silicon, occasionally aluminum*

**Figure V.** The Montmorillonite Lattice Structure. After Grim.



$\text{Al}_2\text{O}_3$	15.56 - 20.27%
$\text{H}_2\text{O}$	14.10 - 22.84%

Most of the montmorillonites possess varying but slightly larger percentages of the same oxides as those found in the kaolinites. Variation in the actual and theoretical chemical composition is due chiefly to substitution in the lattice, e.g. Mg for Al, Al for Si, etc.

Illites.. The group name Illite was suggested by Grim<sup>11</sup>, Bray and Bradley to define clay minerals which are similar but not identical to the white micas. As shown in Figure VI the lattice structure is practically the same as that for montmorillonite, the chief differences being the replacement of some of the silicons by aluminum with the resulting charge deficiency being balanced by potassium ions. In many of the well crystallized examples, one fourth of the silicons are replaced by aluminum ions. The potassium ion is found between unit lattice structures where it fits into spaces between the oxygen atoms. The presence of the potassium ion improves the bond existing between the unit layers of the illites. Illites lie between the montmorillonites and kaolinites in regard to stability and exchange capacity. Quantitative analyses of just two Illites by the API<sup>1</sup> produced the following results:

$\text{SiO}_2$	56.91 - 57.41%
$\text{Al}_2\text{O}_3$	17.96 - 18.50%
$\text{K}_2\text{O}$	5.10 - 5.75%
$\text{H}_2\text{O}$	8.84 - 9.67%

Many clays classed as white micas or in the other major clay mineral groups under older classifications would probably be more properly listed under the illites.



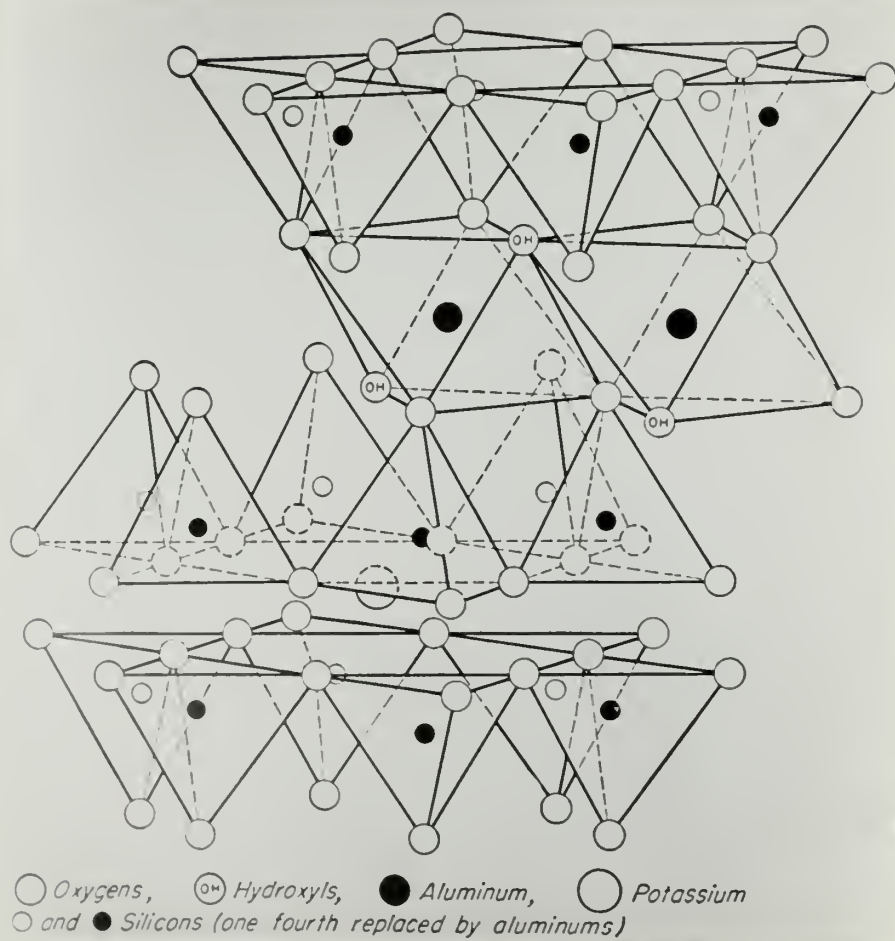


Figure VI. The Illite Lattice Structure  
After Grim.





PART III  
EXPERIMENTAL PROCEDURES

A. Instrumentation

A Perkin-Elmer Corporation Model 21 double beam recording infrared spectrophotometer was utilized in obtaining the spectra for this report. The instrument makes direct reading transmission records on 34" x 11" charts plotting percent transmission versus wavelength in microns, or wave numbers in reciprocal centimeters. Without alteration the instrument will plot absorbance (optical density) versus wavelength or wave numbers. With suitable gears replacing the standard set, the instrument will record spectra directly on National Research Council spectrum cards, IBM cards, graph paper, etc. The basic instrument is shown in Figure VII. Not shown are the separate amplifier and power supply which are usually located in cabinets beneath the table on which the instrument rests. The instrument is approximately four feet in overall length.

The double beam principle automatically accounts for variables which would otherwise require separate corrections if the double beam were not used. Two cells, one containing a window with the sample to be tested along with the substance in which it is suspended and the other cell containing a window with only the suspending medium are mounted in the instrument, each intercepting one of the beams from the infrared source. The sample cell beam will vary due to the combined effects of the sample, the suspending medium and air, while the other cell will vary due to the effect of only the suspending medium and air.





Figure VII Double Beam Recording Infrared Spectrophotometer. (Photograph Courtesy Perkin Elmer Corporation).



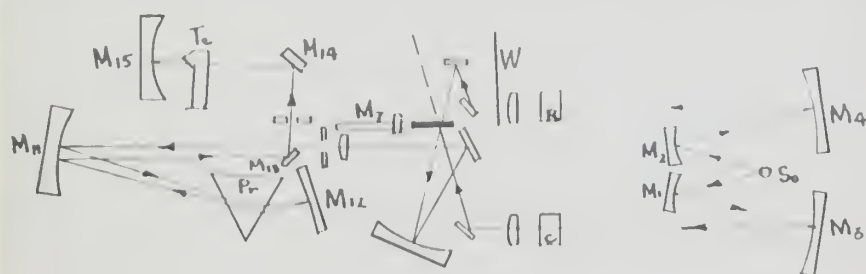


Figure VIII. Optical layout of spectrophotometer.



The optical layout of the instrument is shown in Figure VIII.

Two beams of light from the same source  $S_0$ , a Nernst Glower, are focused by mirror pairs  $M_1 M_3$  and  $M_2 M_4$  into the sample cell  $C$  and a reference cell  $R$ . The reference beam also passes through wedge aperture  $W$  which rolls in and out of the optical path serving to equalize the intensity of the reference beam with that of the sample beam. The sample beam and reference beam are combined by means of a rotating sector mirror  $M_7$  which alternately transmits the reference beam through the cut out sector and reflects the sample beam by the solid silvered sector through a monochromometer which selects by means of the prism  $Pr$  and Littrow mirror  $M_{12}$  the particular wavelength of infrared radiation being scanned and ultimately transmitted.

The instrument is designed to use prisms of rock salt, lithium fluoride, and potassium bromide depending on which portion of the spectra is to be investigated. The rock salt prism was used throughout the runs reported in this thesis.

After passing through the prism, the beam is transmitted to a detector  $T_c$  via mirrors  $M_{11}$   $M_{13}$   $M_{14}$  and  $M_{15}$ . If the reference and sample beams are of equal intensity, i.e.: no absorption, no output is observed from the detector. Inasmuch as the instrument is transmitting beams of radiation which are not visible, it is not possible to use a detector sensitive only to visible radiation. A thermocouple detector of extremely high sensitivity is therefore utilized. For the instrument to have an error limited to no more than  $\frac{1}{2}$  of one per cent, the thermocouple must be sensitive to changes in temperature corresponding to  $0.005^\circ$  Centigrade.

As seen in the block diagram, Figure IX, the output of the detector is amplified and passes through circuits controlling the servo







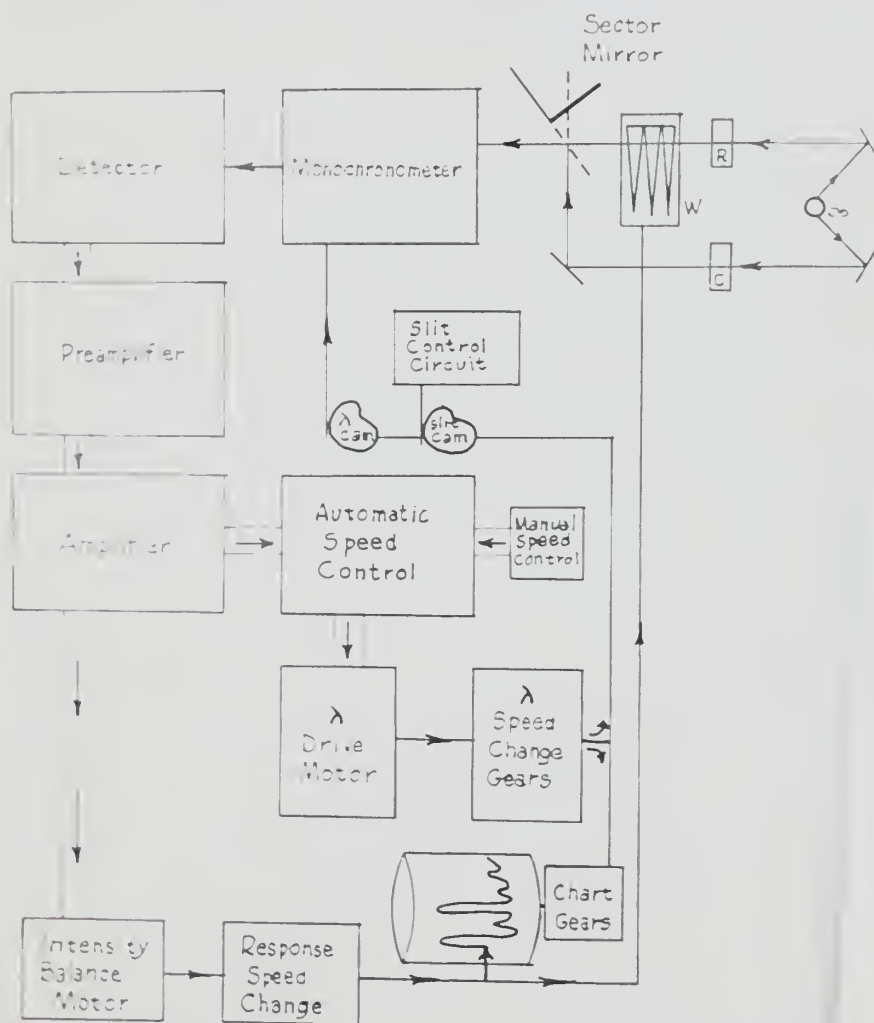


Figure IX. Block diagram of spectrophotometer



motor which operate the wedge aperture W balancing the beam intensities. The amplifier also feeds impulses to the recording drum speed controls which are linked electrically with the monochronometer so that the wavelength being refracted and transmitted by the prism corresponds to that on the chart of the recording drum. The drum operating speed can be varied to suit the degree of accuracy and response desired for the particular sample being examined. The range of scanning speeds varies from .25 minutes to 900 minutes per micron.

Operation of the instrument is simple, requiring no special knowledge or ability. After turning the instrument on, it is only necessary to insert the sample and reference cells, place the desired chart on the drum and align the chart to correspond with the starting wavelength appearing on the wavelength register (usually two microns). The drum spindle is tightened, the scanning speed adjusted as desired, and the scanning start switch is pressed. The rest of the operation is automatic. The instrument, unattended, will plot the desired spectrum and then turn itself off at approximately 15.5 microns. After each run, the instrument is reversed and reset to the two micron wavelength setting. This operation is done manually.

The machine incorporates in its design an automatic supressor which, if switched into operation will automatically slow down the scanning speed whenever a significant change in absorption occurs. Narrow bands which might otherwise be obscured at fast operating speeds are thus detected automatically.

With suitable cells, samples of gas, liquid, or solids may be studied. Suspending mediums commonly used for solid samples similar to



the clay minerals include Mujol, white mineral oil, perfluorokerosene, and potassium bromide.

### B. Materials

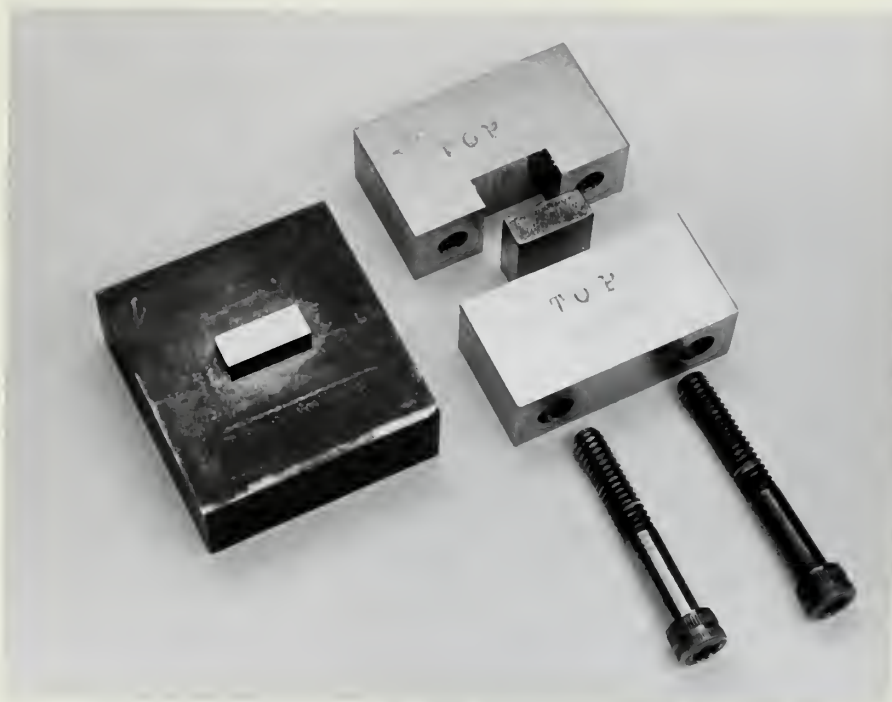
Most of the clay minerals tested were those collected and identified by the American Petroleum Institute in conjunction with their research project number 49. These specimens and the other clay minerals used are distributed by the Ward's Natural Science Establishment in Rochester, New York. The natural clays tested were supplied through the courtesy of the New York State Soil Testing Laboratory in Latham, New York.

Sample and reference cells (or windows) were prepared using the potassium bromide technique described in detail in the section on Procedures. The potassium bromide used is optical quality prepared especially for infrared applications by the Harshaw Chemical Company, Cleveland 6, Ohio.

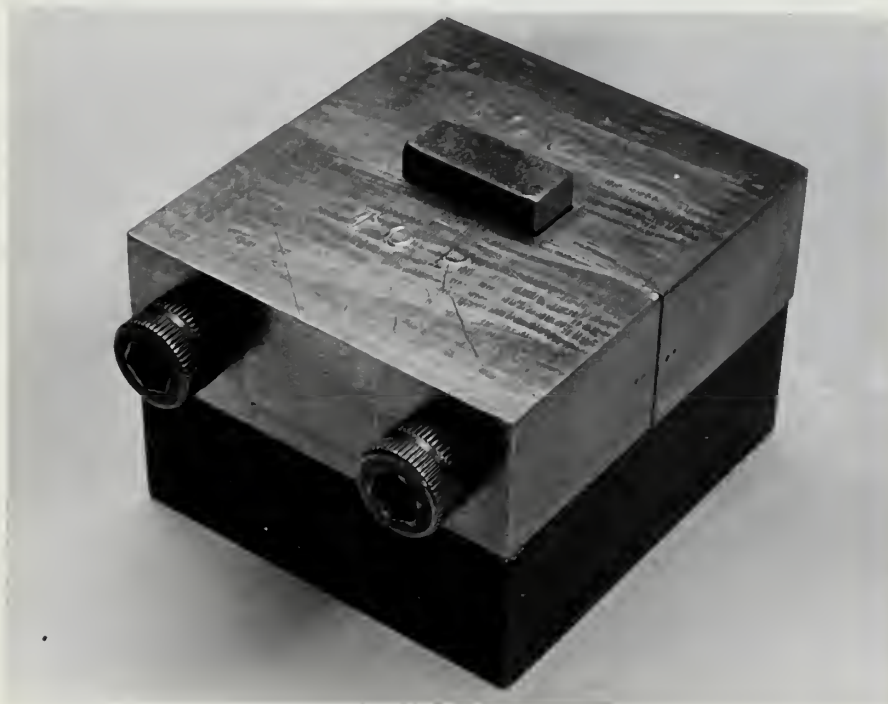
The die used in preparing sample and reference windows shown in Figure X was fabricated in a local machine shop and hardened in equipment of the R.P.I. Department of Metallurgy after it was determined that the pressures necessary for satisfactory windows exceeded the proportional limit of the unhardened steel. A rectangular window  $1/4$  inch by  $39/64$  inch is produced using this type of die. Discussions concerning a different type of die are included in the Recommendations section of this thesis.

Printed charts plotting transmittance (% transmission) versus wave numbers and wavelength were used for all spectra. These charts designed specifically for the spectrophotometer used are available from





KBr window die disassembled



KBr window die assembled  
Figure X







the Perkin-Elmer Corporation, Norwalk, Connecticut as their form number 021-6310.

### C. Procedures

#### Preparation of Clay Mineral Samples

Two methods were used in preparing clay mineral samples for infrared analysis. The method used for the bulk of the curves run will be referred to as the standard method, while that used at the end of the experimental work will be referred to as the amalgamator method.

Standard method. As shown in Figure XI the clay mineral specimens as received from the supplier varied from large rock-like pieces three or four inches in size to fine powder which would readily pass a 200 mesh sieve. Large samples were broken down in a standard mortar-and-pestle and ultimately ground to a fine powder in a small agate mortar. The samples were oven dried at 105° Centigrade for a period of 24 hours. After cooling, the powder was then passed through a 325 mesh sieve and placed in a desiccator until required for preparing sample windows. The time required to reduce the samples sufficiently to pass a large enough quantity for a window through the 325 mesh sieve varied from just a few minutes to as long as forty minutes for certain of the Bentonites.

To eliminate the undesirable bands caused by the use of various organic suspending mediums, the potassium bromide technique was employed to prepare the windows.<sup>7, 13, 15</sup> The die used for making the windows requires approximately 100 milligrams of potassium bromide to produce a window of the desired thickness.

In the standard method of sample preparation, two to three milligrams of clay passing the 325 mesh sieve were used in each window.



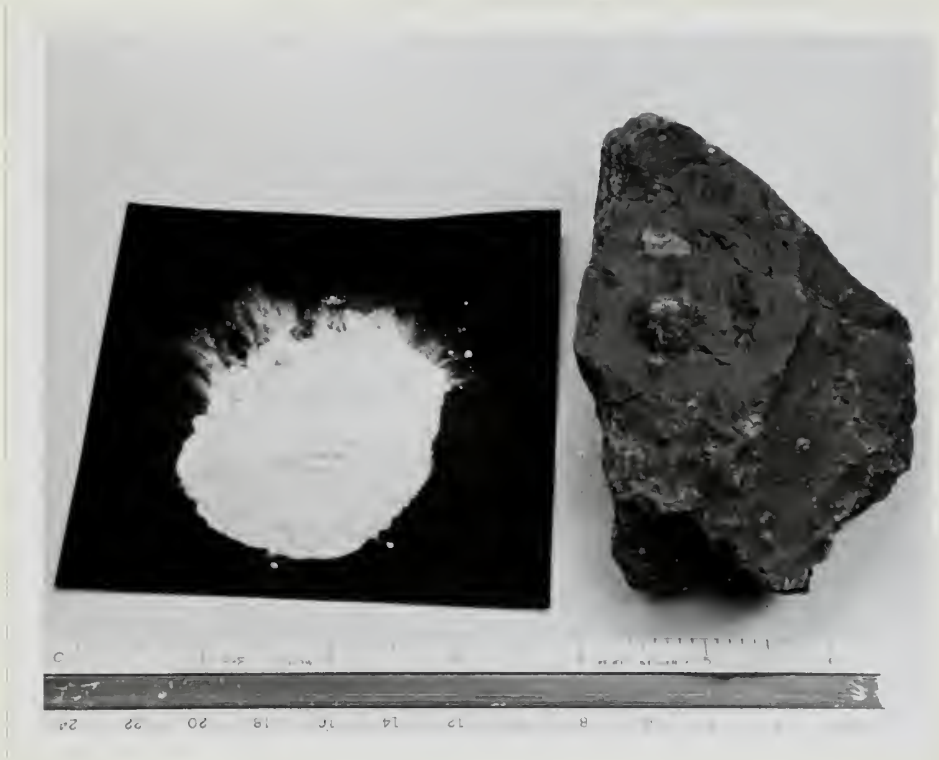


Figure X. As received clay minerals showing size range.



The potassium bromide was first dried for 24 hours in an oven at 105° Centigrade and then ground in the mortar to a powder. One hundred milligrams of the potassium bromide was then weighed out on a cover glass by means of an analytical balance. By means of a nickle spatula two to three milligrams of clay mineral was added to the potassium bromide. The mixture was placed in a small glass container and intimately mixed with a glass rod. The container with sample was immediately placed in a desiccator until it could be pressed into a window in the die. Precautions must be taken to ensure that the clay and potassium bromide remain in the air for as short a time as possible. The spectra curves are greatly effected by any water vapor taken up by the potassium bromide. Potassium bromide is corrosive to metals if allowed to remain in contact over extended periods.

Amalgamator method. Clay mineral samples mixed in the dental amalgamator procured by the Department of Chemical Engineering required a special technique to produce satisfactory infrared spectra. Optimum results were obtained using 0.8 milligram of clay and 100 milligrams of potassium bromide. A small quantity of clay mineral (3 milligrams or less) was weighed out as accurately as permitted by the analytical balances used. At least 0.8 milligram of clay was required. Sufficient potassium bromide was added to the clay to give the desired 8/10th per cent mixture. Because of the pulverizing qualities of the amalgamator, the clay minerals did not require grinding as long as a quantity in the range of 0.8 to 3 milligrams could be weighed out. A single grain of clay would be satisfactory. After mixing in the amalgamator the resulting powder was weighed out in 100 milligram quantities and stored to





await window preparation.<sup>28</sup>

#### Preparation of Potassium Bromide Windows

A hydraulic press capable of exerting a pressure of twenty thousand pounds on the die was required to press out satisfactory windows using the KBr technique. Such a press is shown in Figure XII with the die in place during the pressing of a window.

The die was cleaned thoroughly and assembled without the plunger. The set screws were tightened sufficiently to hold the plunger guide pieces firmly against the base block. The clay mineral and KBr mixture prepared as described previously was poured into the die using care to insure that none of the sample would be lost. After spreading the mixture out evenly over the bottom of the plunger hole by means of a small spatula the plunger was inserted and the die then placed in the hydraulic press. A hardened steel plate was inserted between the top of the plunger and the upper bearing plate of the press to distribute the pressure on the plunger over a larger surface. The cross sectional area of the plunger is 0.1523 square inch which with a 20,000 pound load on the press causes a unit stress of 131,000 pounds per square inch, considerably in excess of that which can be handled by all but the highest quality hardened steels.

The window was held under twenty thousand pounds pressure for five minutes after which time the pressure was slacked off slowly (15 seconds) and the die removed from the press.

The die was carefully disassembled to prevent damage to the extremely fragile window. A window will generally average about 20 microns in thickness. The design of the die was such that the windows.





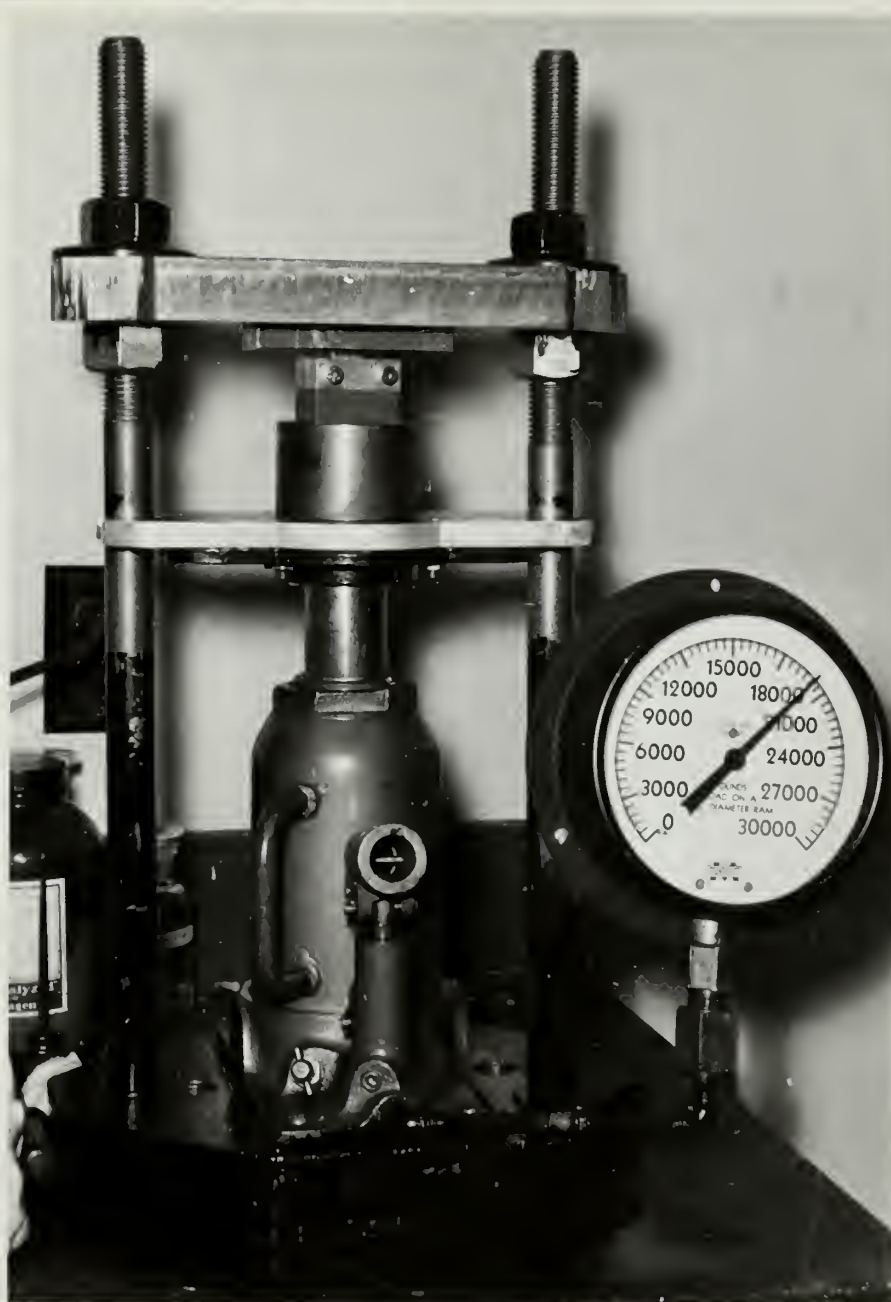


Figure XII. Sample die in hydraulic press

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would be held tightly in the U shaped portion of the plunger guide. The rectangular shape of the window appeared to result in the development of stress concentrations in the corners of the plunger guide which would result in considerable difficulty in removing the window intact. Of approximately 120 windows prepared for this thesis at least fifty were cracked and broken in removing them from the die. Of the fifty broken, about half were usable in producing satisfactory spectra. For the qualitative results desired in this work, the only criteria for a satisfactory window was that enough window be mounted in the holder to cover the slit opening of the spectrophotometer. Stress cracks or actual breaks did not affect the spectrum as long as the slit was covered. Windows which were broken into two pieces could be used as long as they were capable of being mounted in the cell holder.

A sharp razor blade was used to cut out the window from the U shaped plunger guide. The plunger was gently held against the window and the razor blade then used to cut the window away from the three binding edges. Cutting was performed from the lower or under side of the plunger guide. Generally cutting through the two ends of the window was all that was required to dislodge the window; however, in some instances it was also necessary to cut the window away from the back edge of the guide.

After a window was removed from the die, it was immediately placed in an identifying envelope and placed in a portable desiccator. The windows were handled by tweezers. If the window is pressed in the same location as the spectrophotometer, the use of the portable desiccator is unnecessary; however, in this case the windows were pressed in one building and transported to another for running, making the procedure

The first of these is the fact that the  $\text{H}_2\text{O}$  vapor pressure is not constant, but varies with temperature. At a temperature of  $100^\circ\text{C}$ , the vapor pressure of water is  $1013\text{ mm Hg}$ . At a temperature of  $20^\circ\text{C}$ , the vapor pressure of water is  $17.5\text{ mm Hg}$ . This means that at  $100^\circ\text{C}$ , the partial pressure of water vapor is  $1013\text{ mm Hg}$ , and at  $20^\circ\text{C}$ , the partial pressure of water vapor is  $17.5\text{ mm Hg}$ . This is a significant difference, and it must be taken into account when calculating the partial pressures of the other gases in the mixture.

The second of these is the fact that the  $\text{H}_2\text{O}$  vapor pressure is not constant, but varies with temperature. At a temperature of  $100^\circ\text{C}$ , the vapor pressure of water is  $1013\text{ mm Hg}$ . At a temperature of  $20^\circ\text{C}$ , the vapor pressure of water is  $17.5\text{ mm Hg}$ . This means that at  $100^\circ\text{C}$ , the partial pressure of water vapor is  $1013\text{ mm Hg}$ , and at  $20^\circ\text{C}$ , the partial pressure of water vapor is  $17.5\text{ mm Hg}$ . This is a significant difference, and it must be taken into account when calculating the partial pressures of the other gases in the mixture.

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mandatory.

### Preparation of Windows for Special Purposes

Effect of particle size. One set of windows was prepared by the standard methods. Another set was prepared in a similar manner except that the clay minerals were passed through a 200 mesh sieve and retained on a 325 mesh sieve. This procedure resulted in a particle size distribution from 44 to 74 microns in size.

Effect of varying sample quantity. Windows were prepared by the standard method using varying quantities of the same clay mineral, an H-5, kaolinite, from Bath, South Carolina. Windows were prepared using 4-5 milligrams and 0.5-1.5 milligrams in addition to the standard range of 2-3 milligrams. The amount of KBr was left constant at 100 milligrams.





## PART IV.

## RESULTS AND DISCUSSION

A. GeneralPurpose

The purpose of this part of the thesis is to describe in detail the results of the investigation and to compare the reference clay mineral spectra obtained using the KBr disk technique with those obtained by the several investigators of the American Petroleum Institute.<sup>1</sup>

Conclusions derived from the results as well as recommendations for further work will be included in the next following separate parts of this report.

Window Preparation

The techniques followed in preparing windows for infrared analysis were described in Part III C under procedures. Two variables occur in the actual pressing of windows in the die, namely: length of time under pressure and the magnitude of the applied pressure. Recommendations in the literature concerning the length of time pressure should be applied ranged from five to twenty minutes while those concerning the pressure range varied from 1000 to 100,000 pounds per square inch.<sup>13,15,18,28</sup> Initial attempts to produce satisfactory windows failed largely because of the use of pressures much too low. The stressing of lengthy times under pressure by one investigator, in order to produce windows of the desired transparency, resulted in the first attempts being run for twenty minutes. Because of the low pressures used (three tons per square inch) as recommended, the windows produced were completely unsatisfactory. In most cases under these conditions only a small part of the windows were





transparent, the rest being completely opaque, resembling the white powdered KBr, and lacking any strength. Regardless of the care taken in handling, these windows would usually break into pieces or flake off into powder. Window quality improved with increasing pressure. A pressure of 15,000 pounds on the die (99,000 pounds per square inch) applied for ten minutes produced completely satisfactory windows. The effect of increasing pressures to 20,000 pounds (131,000 pounds per square inch) for a period of five minutes was then studied. Windows equally as satisfactory as those produced at 15,000 pounds in ten minutes resulted. There appeared to be no advantage to using times longer than ten minutes at the 15,000 pound pressure or longer than five minutes at the 20,000 pound pressure; however, times significantly less than ten minutes at the 15,000 pound pressure resulted in windows of reduced transparency.

#### KBr Spectrum

Two characteristics of KBr make this compound exceptionally useful in infrared analysis of finely divided solids. It will readily flow under high pressure to form a clear solid of sufficient structural strength to permit necessary handling. In addition, as seen in Figure XIII, 1\*, its spectrum is void of absorption bands in the 2-15.5 micron range over which most infrared analyses are performed. Most of the deviations in the KBr spectrum shown are due to "noise" in the spectrophotometer rather than characteristic atomic vibration. The theoretical KBr spectrum is a straight line.

KBr which has not been oven dried will give the characteristic

\*The spectra shown in Figures XIII - XXXII inclusive are numbered 1-4 or 1-3 from top to bottom of each figure.



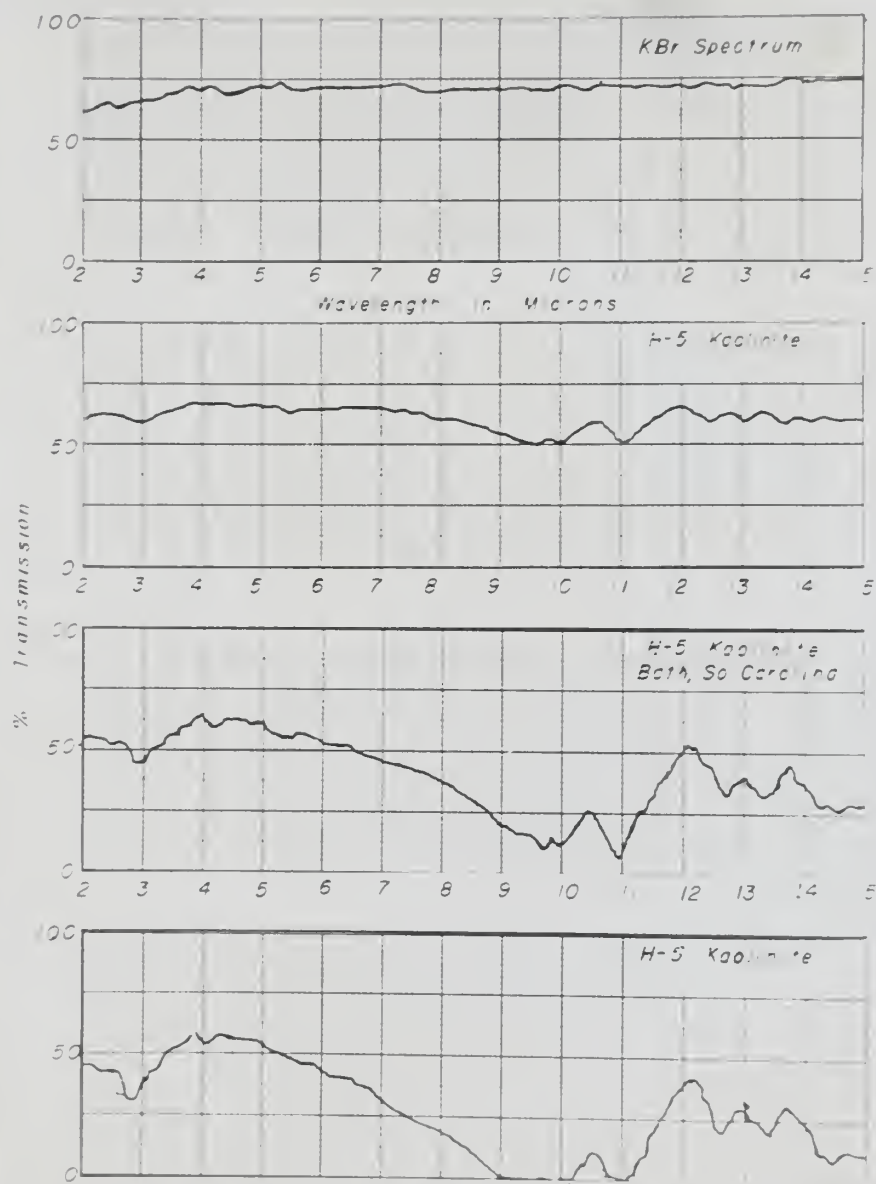


Figure XIII. Infrared Spectra showing KBr spectrum and effect of varying sample quantity.



water bands at 2.9 and 6 microns. In all of the windows prepared for this report the KBr was oven dried for no less than 24 hours at 105° Centigrade.

#### Variations in Sample Quantity

Curves 2, 3, and 4 of Figure XIII have been included to illustrate the effect of varying the quantity of clay minerals used in the preparation of sample windows. In curve 2 a range of 0.5 to 1.5 milligrams of H-5 kaolinite was used. The resulting spectrum shows only weak absorption bands and in certain instances there would be difficulty in separating the bands from the normal machine "noise" caused by the response and sensitivity characteristics of the spectrophotometer.

In curve 3 a range of 2-3 milligrams of clay was used. The results in this range were the most satisfactory with the absorption bands being sufficiently strong to permit accurate qualitative identification of the clay mineral. A better idea of the relative intensity of the different bands is also indicated.

In curve 4 a range of 4-5 milligrams of clay was used. In this spectrum all bands are more intense but in the 9-11 micron range of wavelength, absorption was so complete as to conceal some of the detail of the spectrum.

The above quantities were used in the standard method of window preparation described under Part III C, Procedures. In using the amalgamator method, it was found that the optimum amount of sample decreased from 2-3 milligrams as above to 0.8 milligrams. Additional information concerning the amalgamator method is included in Part IV C.





### Variation in Particle Size.

Where the particle size of a sample equals the wavelength of infrared radiation being scanned, strong selective scattering of the radiation occurs.<sup>20</sup> Where this occurs, the percent transmission is reduced affecting the overall spectra and giving the appearance of weak absorption bands. The effect of particle size was investigated by preparing samples as described in Part III C, Procedures. Spectra were run on H-36, illite, with particle distribution between 44 to 74 microns and also from 44 microns and smaller. In all cases the variations when compared with curve 3 of Figure XX was negligible. Results from this portion of the investigation were considered to be inconclusive.

### B. Reference Spectra

Figures XIV through XX inclusive are infrared spectra of reference clay minerals that were collected and identified for the American Petroleum Institute Research Project Number 49.<sup>1</sup> The spectra results generally check those reported by the several investigators of Project 49.

The shape of the spectra produced in this investigation more closely resemble the results of Bray and Stevens while differences were evident in the shapes of those of Adler, Hunt, Keller and Pickett.

Curves produced by Bray and Stevens appear to have more clearly defined absorption bands with the regions on each side of the bands having higher transmission percentages. In most of the curves produced in the early part of this investigation from hand mixed samples a gradual decrease in transmission (or increase in absorption) occurred in the 7.5 to 10 micron wavelength range. The increased absorption occurring in

1911. Vol. 41. Part 1. (The Journal of the Royal Anthropological Institute, 1911, Vol. 41, Part 1, pp. 1-100.)

The first part of the volume contains the following papers:—  
1. The Journal of the Royal Anthropological Institute, 1911, Vol. 41, Part 1, pp. 1-100.

2. The Journal of the Royal Anthropological Institute, 1911, Vol. 41, Part 1, pp. 101-200.

3. The Journal of the Royal Anthropological Institute, 1911, Vol. 41, Part 1, pp. 201-300.

4. The Journal of the Royal Anthropological Institute, 1911, Vol. 41, Part 1, pp. 301-400.

5. The Journal of the Royal Anthropological Institute, 1911, Vol. 41, Part 1, pp. 401-500.

6. The Journal of the Royal Anthropological Institute, 1911, Vol. 41, Part 1, pp. 501-600.

7. The Journal of the Royal Anthropological Institute, 1911, Vol. 41, Part 1, pp. 601-700.

8. The Journal of the Royal Anthropological Institute, 1911, Vol. 41, Part 1, pp. 701-800.

9. The Journal of the Royal Anthropological Institute, 1911, Vol. 41, Part 1, pp. 801-900.

10. The Journal of the Royal Anthropological Institute, 1911, Vol. 41, Part 1, pp. 901-1000.

11. The Journal of the Royal Anthropological Institute, 1911, Vol. 41, Part 1, pp. 1001-1100.

12. The Journal of the Royal Anthropological Institute, 1911, Vol. 41, Part 1, pp. 1101-1200.

13. The Journal of the Royal Anthropological Institute, 1911, Vol. 41, Part 1, pp. 1201-1300.



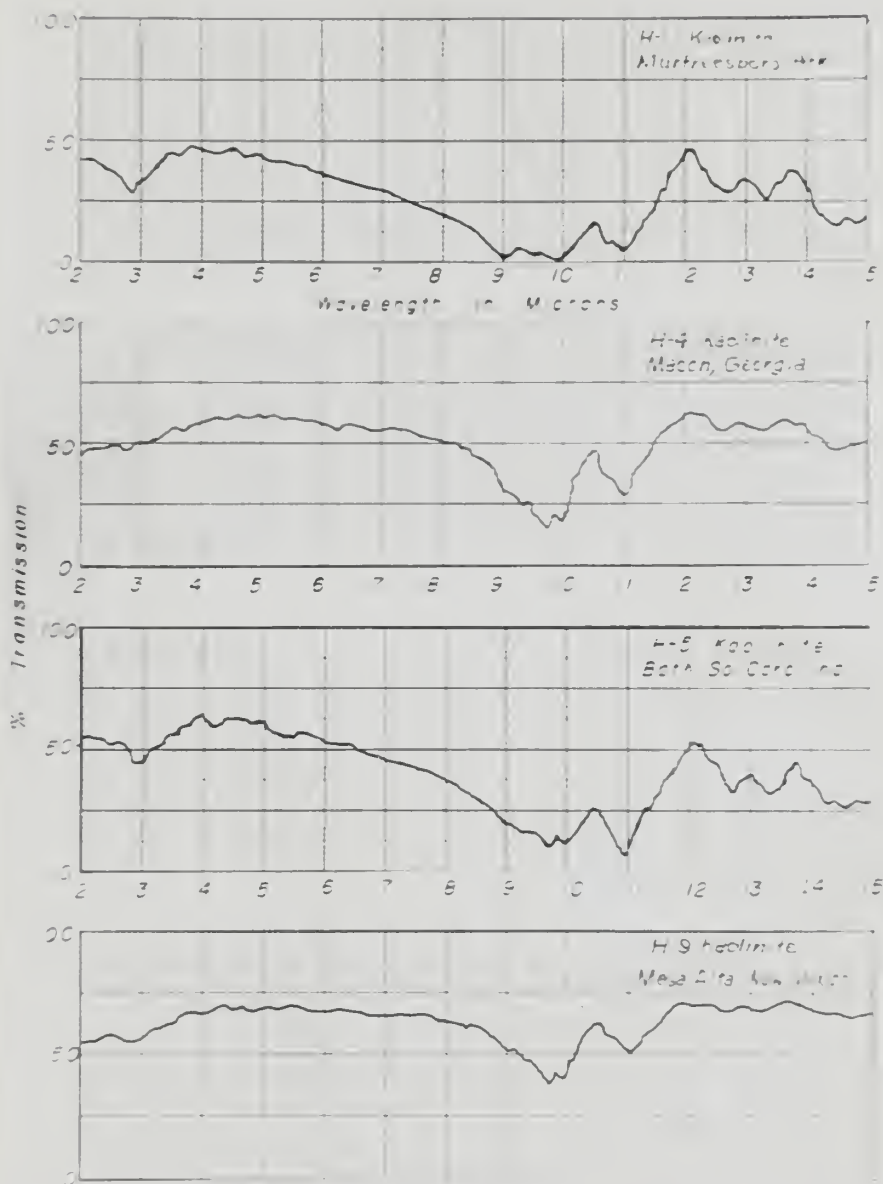


Figure XIV. Spectra of 1:1 lattice clay minerals  
Kaolinites



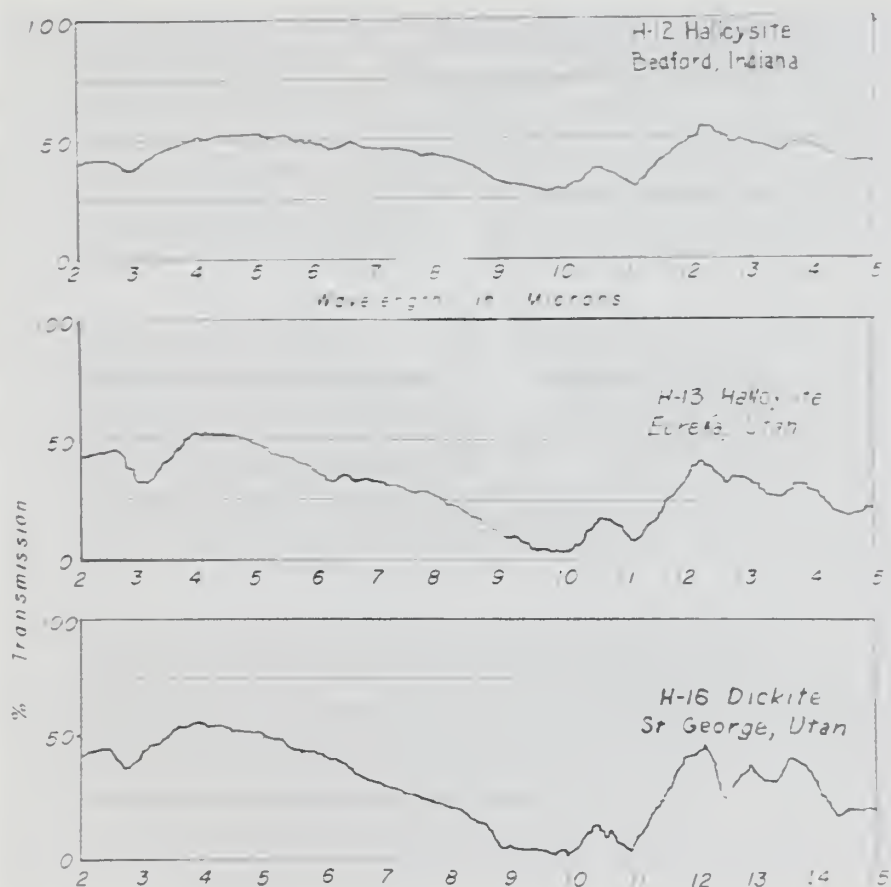


Figure XV. Spectra of 1:1 lattice clay minerals  
Halloysites and Dickite



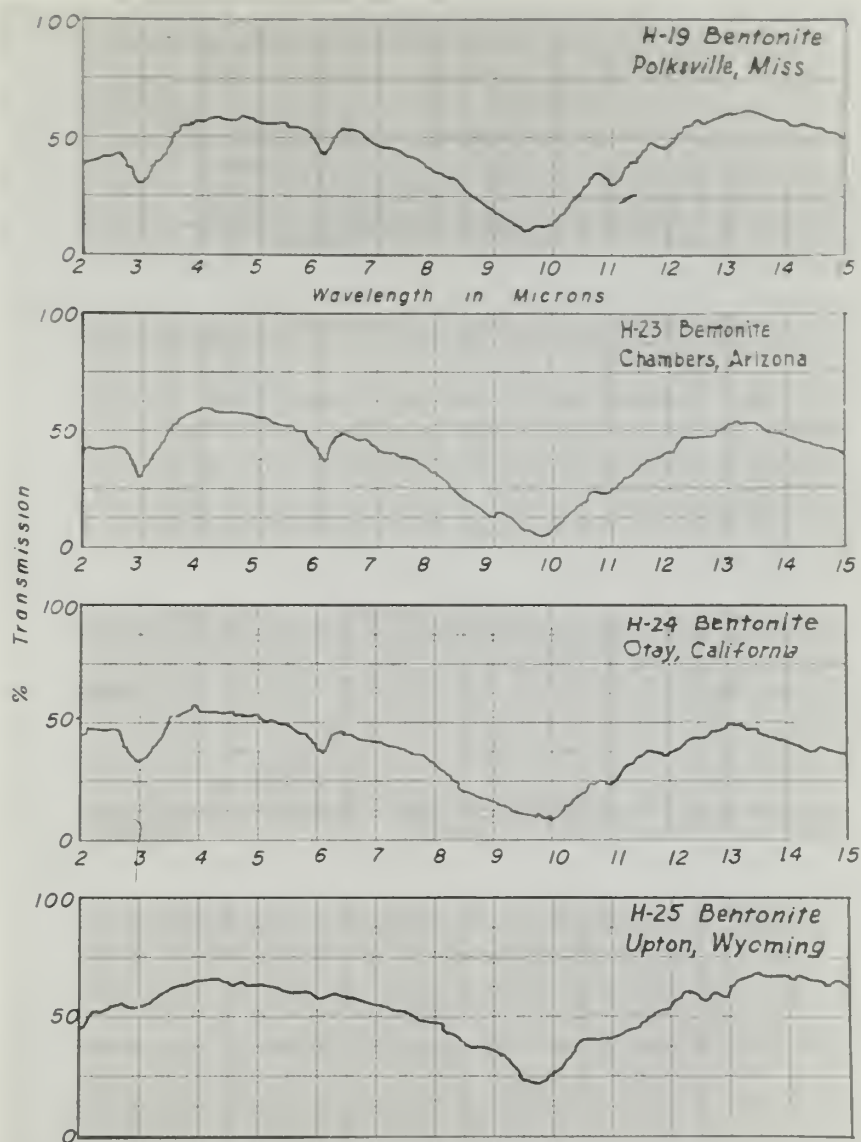


Figure XVI. Spectra of 2:1 lattice clay minerals  
Bentonites



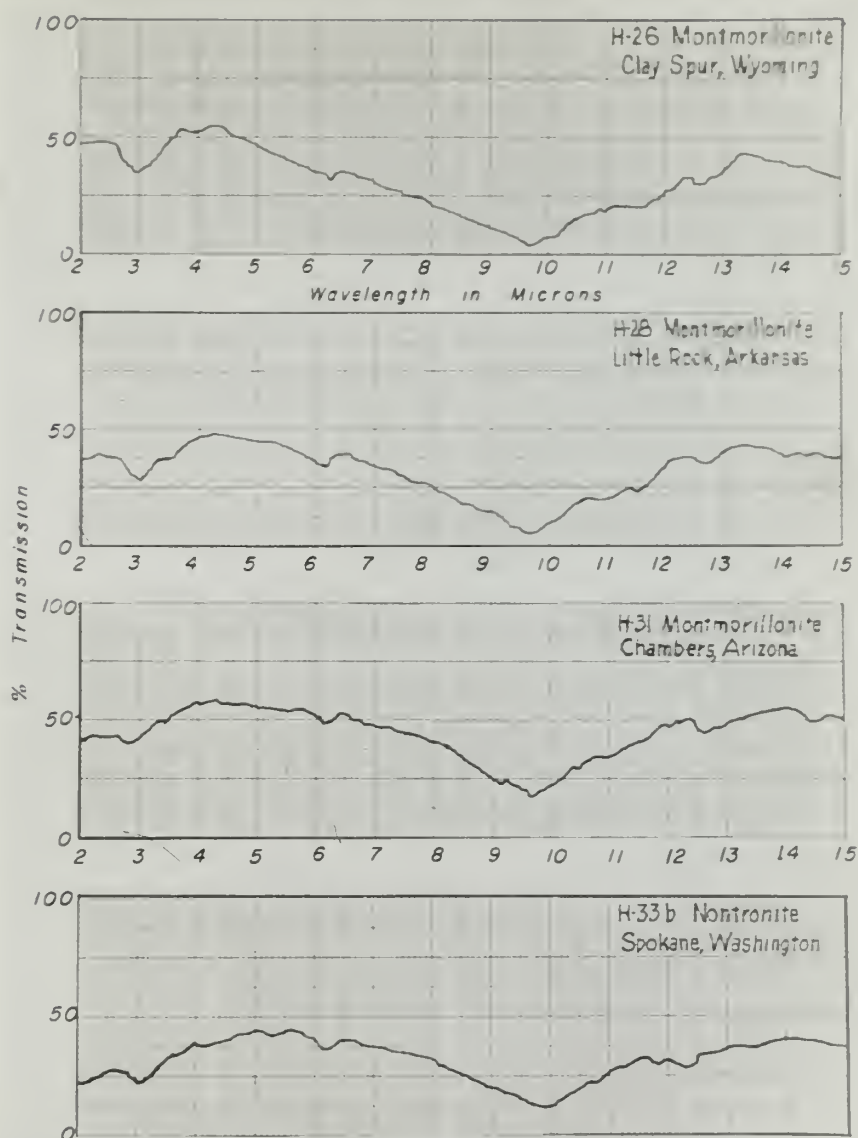


Figure XVII. Spectra of 2:1 lattice clay minerals  
Montmorillonites and Nontronite





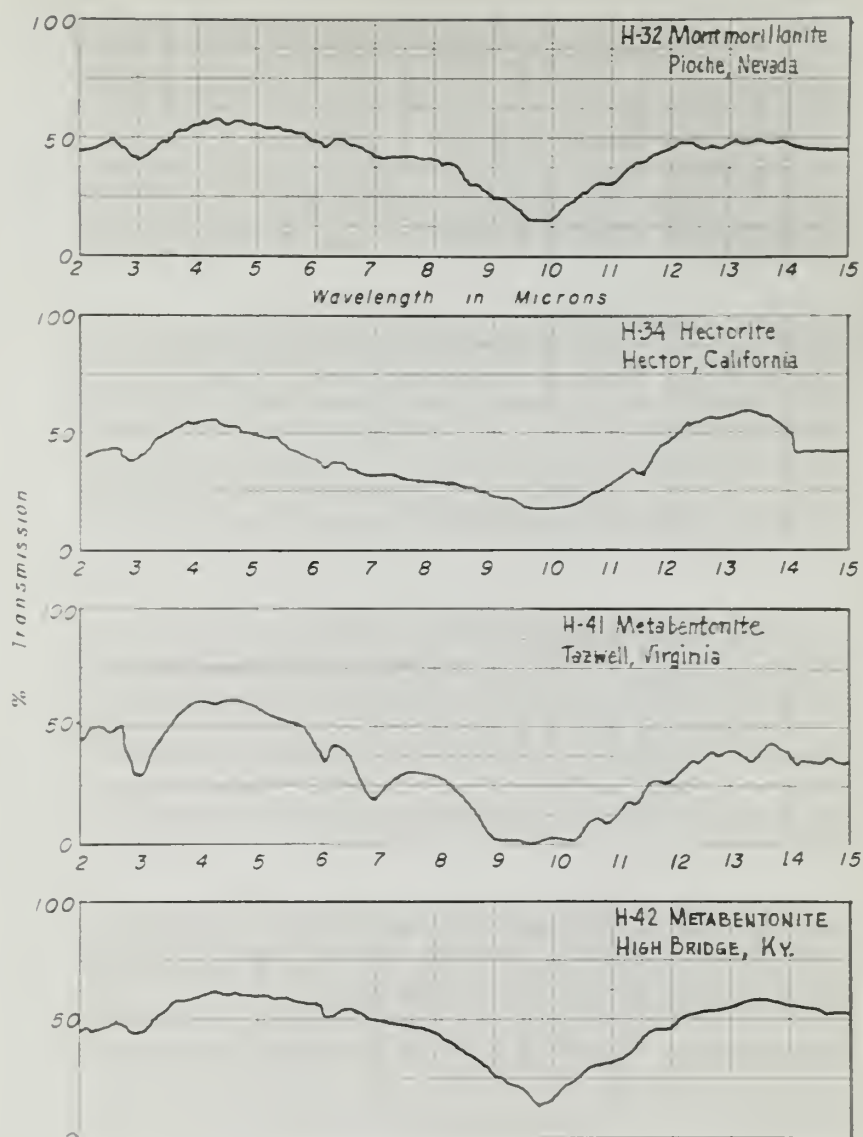


Figure XVIII. Spectra of 2:1 lattice clay minerals Montmorillonite, Hectorite and Metabentonites.



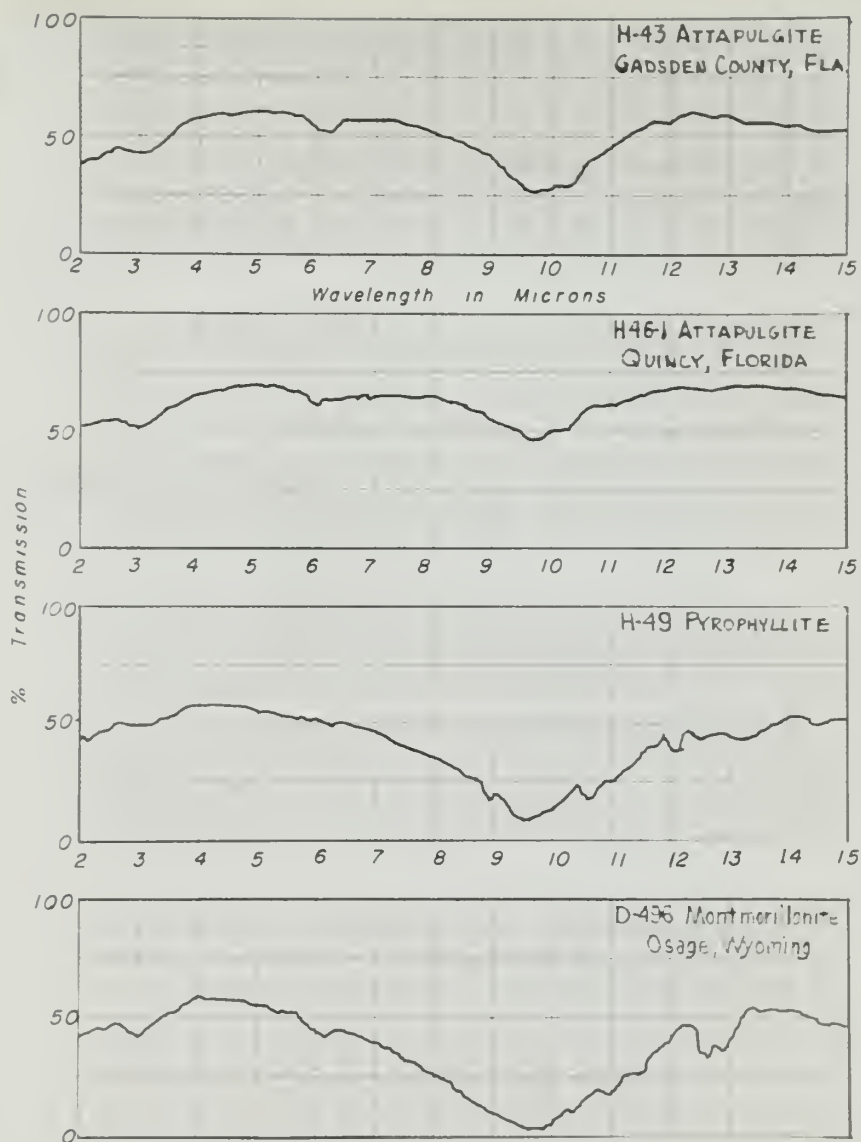


Figure XIX. Spectra of 2:1 lattice clay minerals Attapulgites, Pyrophyllite, Montmorillonite.



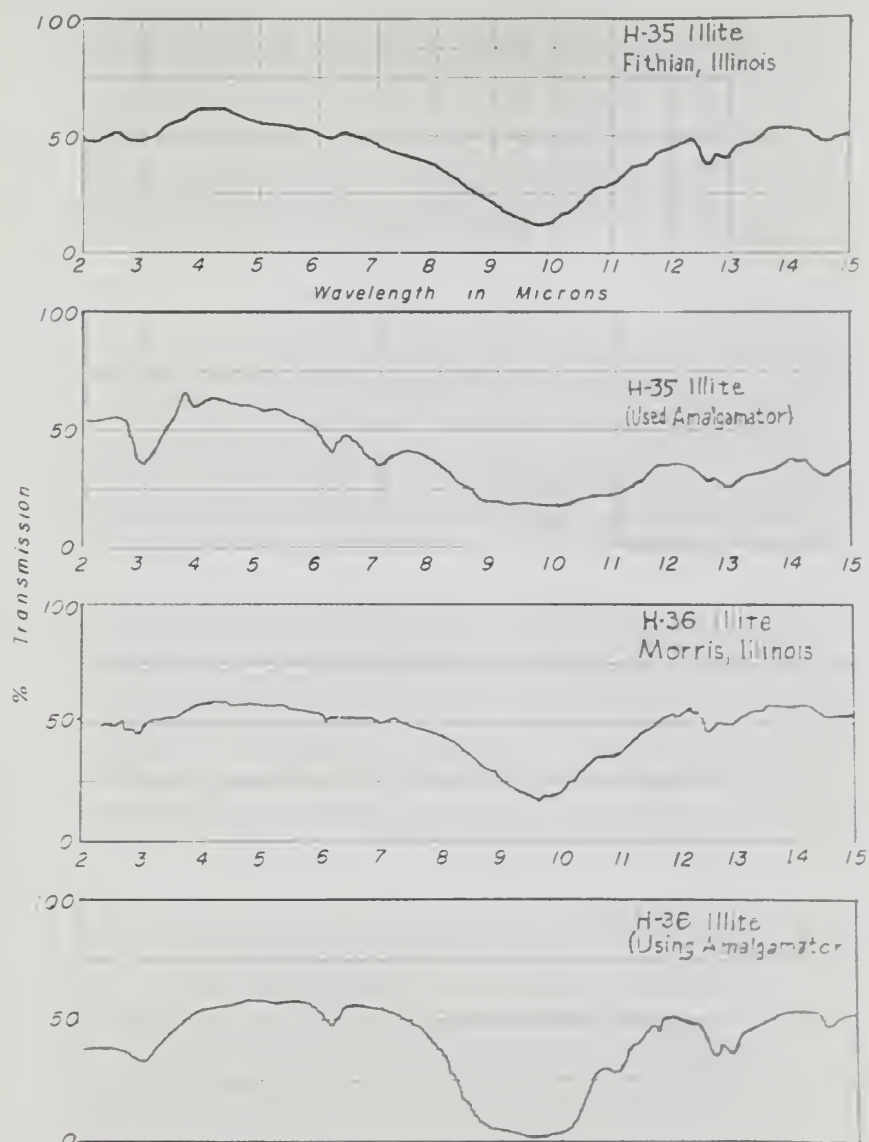


Figure XX. Spectra of 2:1 Lattice Clay Minerals Illites



this region is attributed to scattering caused by particle sizes corresponding to the 7.5 - 10 micron wavelength of infrared radiation.

Although considerable variation did exist in the shape of spectra produced by the different API investigators and in those produced for this investigation, the band center positions which resulted from the different investigations varied only slightly. More variation than actually occurred could be reasonably expected, considering the variations in technique and the differences in homogeneity which are bound to exist in even these relatively pure clay mineral samples.

Table 1 shows the position of band centers resulting from this investigation. Table 2 shows the band centers for the three major clay minerals after the data produced by Hunt.<sup>1</sup> Similar information is given in Table 3 and was averaged and condensed from the results of Keller and Pickett.<sup>1</sup>

The position of band centers rather than the shape of a given spectrum would appear to be the most important criteria in applying infrared analysis to identifications of unknowns particularly where investigative techniques are not similar.

### C. Use of Amalgamator

The use of a dental amalgamator to prepare sample mixtures for the KBr window technique was suggested by Kirkland<sup>28</sup> in October 1955. The procurement of such a device was considered by the writer early in the investigation but due to the results obtained on the effect of particle size (Part IV A) and a limitation on available funds, the idea was abandoned; however, such a device did become available through the Depart-





TABLE 1  
POSITIONS OF BAND CENTERS

Clay ID No.	Wavelength Range													
	2	3	4	5	6	7	8	9	10	11	12	13	14	
H-1	2.8						9.0	9.5	9.8	11.	12.7	13.4	14.5	
H-4	2.8*							9.7	10.	11.	12.7	13.3	14.5	
H-5	2.9		4.2					9.7	10.	10.9	12.7	13.3	14.5	
H-9	2.8*							9.7	9.9	11.	12.7	13.2	14.7	
D496	2.9						8.9	9.7	10.7	11.	12.6	13.3	14.5	
H-12	2.8				6.1*			9.7	10.	11.1	12.7	13.4	14.5	
H-13		3.			6.1		8.9	9.5	10.	11.1	12.6	13.4	14.5	
H-16	2.7						8.9	9.8	10.	11.1	12.6	13.3	14.4	
H-19	2.9				6.1			9.5		11.	11.9			
H-23	2.9				6.1		8.9	9.8		10.9	12.*			
H-24		3.			6.1				10.	11.	11.9			
H-25		3.			6.1			9.7			12.6	12.9		
H-26	2.9				6.3			9.7			12.6			
H-28		3.			6.2			9.7		11.5	12.6		14.	



TABLE 1 cont'd

Clay ID No.	2	3	4	5	6	7	8	9	10	11	12	13	14
H-31	2.8				6.1			9.7	10.5		12.7		
H-32		3.			6.2			9.8			12.6	12.9	
D496		3.			6.2			9.7	10.3	11.	12.6	12.9	
H-33b		3.1			6.2			9.9		11.8	12.3		
H-34	2.8				6.1	7.0*		9.9		11.5			14.2
H-35		3.			6.2	7.0		9.8			12.6	12.9	14.6
H-36		3.			6.1	7.0*		9.7			12.6	12.9	14.5
H-41	2.5	3.			6.1	7.0		9.7	10.9	11.4	12.	13.3	14.2
H-42		3.			6.2			9.7			12.		
H-43		3.			6.2			9.7	10.4		12.		
H-46-1		3.			6.			9.7	10.3				
H-49							8.9	9.5	10.6		12.1	13.3	14.5

\*weak



TABLE 2

## POSITIONS OF BAND CENTERS

According to Hunt<sup>1</sup>

Clay Type	2	3	4	5	6	7	8	9	10	11	12	13	14
Wavelength Range (microns)													
Kaolinite (9 types)	2.7						8.9	9.7	10.7		12.5	13.5	14.5
Montmorillonite (9 types)	2.8 to 3.2				6.1	7.5 <sub>w</sub>	8.9	9.6		11.	11.4	12.7	
Illite (2 types)	2.8 to 3.1				6.0 <sub>w</sub>	7.0 <sub>w</sub>	8.9	9.7	10.9		12.	13.3	14.4

TABLE 3

## POSITIONS OF BAND CENTERS

According to Keller and Pickett<sup>1</sup>

Kaolinite (6 types)	2.75						8.9 <sub>w</sub>	9.6	10.7		12.6	13.3	14.5
Montmorillonite (8 types)	2.8				6.1		8.7 <sub>w</sub>	9.3	10.8		12.5		
Illite (2 types)	2.8				6.2	7.0 <sub>w</sub>	8.9 <sub>w</sub>	9.7		11.1	12.5		

w - weak band



ment of Chemistry near the end of the experimental portion of the investigation.

The amalgamator used was manufactured by the Crescent Dental Manufacturing Company, Chicago, Illinois, under the trade name "Wig-L-Bug" Amalgamator. It consists essentially of a sample holder grip mounted eccentrically on the shaft of a small motor, a 0-60 second synchronous motor timer, and two sample holders, one of bakelite and the other of stainless steel. The sample holders are approximately one inch in length and  $3/8$  inch in diameter. Each holder has a small pellet about  $1/8$  inch in diameter and  $3/8$  inch in length of the same material as the holder. The unmixed sample and KBr is placed on one of the holders along with the pellet. The holder is placed in the grip, the timer set and the amalgamator turned on. The high speed motion combined with the vibrating pellet serves to reduce the sample to a highly pulverized intimate mixture. Particle size, although not actually measured, was estimated to be below three microns.

Windows produced from the amalgamated mixtures differed considerably in appearance from those produced by the standard mixing method. In the standard method the individual clay particles were visible as small flecks or specks suspended in the transparent KBr, while in those produced from amalgamated mixtures, the particles were not visible. Instead, the window possessed a color tint corresponding to the color of the clay mineral.

The quantity of clay mineral used was necessarily reduced when the amalgamator was used. The first spectra produced using the amalgamated material started at approximately 50% transmission and at 2.5 microns





dropped sharply to zero transmission remaining there for the rest of the run. A 0.8 milligram quantity produced the most satisfactory spectra and in all of the curves reproduced using this method, this amount was used.

The effect of the amalgamator on the infrared spectra is graphically illustrated in Figures XX, XXI, XXII.

In general the major difference was a significant increase in the intensity of absorption bands. In all cases a measurable increase in the 6.1 micron absorption band of adsorbed water was evident. In most cases an increase in the intensity and breadth of the 2.94 micron OH lattice band was also observed.

In Figure XX a weak band at 3.8 microns and a stronger band at 7 microns appeared in the H-35, illite, spectrum which were not visible in the standard method spectrum. Also in Figure XX, the quartz doublet occurring between 12.5 and 13 microns is much more clearly defined in the spectrum for H-36, illite, when the amalgamator was used.

In most of the curves illustrating the amalgamator method the spectra possess steeper portions as absorption bands are approached. This is particularly noticeable in curves 3 and 4 of Figure XX in the range of 7 to 10 microns. In the standard H-36 spectrum a gradual decrease in transmission occurs from 7-10 microns, while in the other H-36 spectrum the curve drops off more rapidly from 7.5-8.5 microns after remaining fairly constant. At about 10.2 microns the transmission increases sharply upward to 10.5 microns.

This shape of curve more closely resembles the curves of Bray and Stevens.<sup>1</sup> As pointed out in Part IV B the gradual transition from high to low transmission in this investigation was interpreted to be due



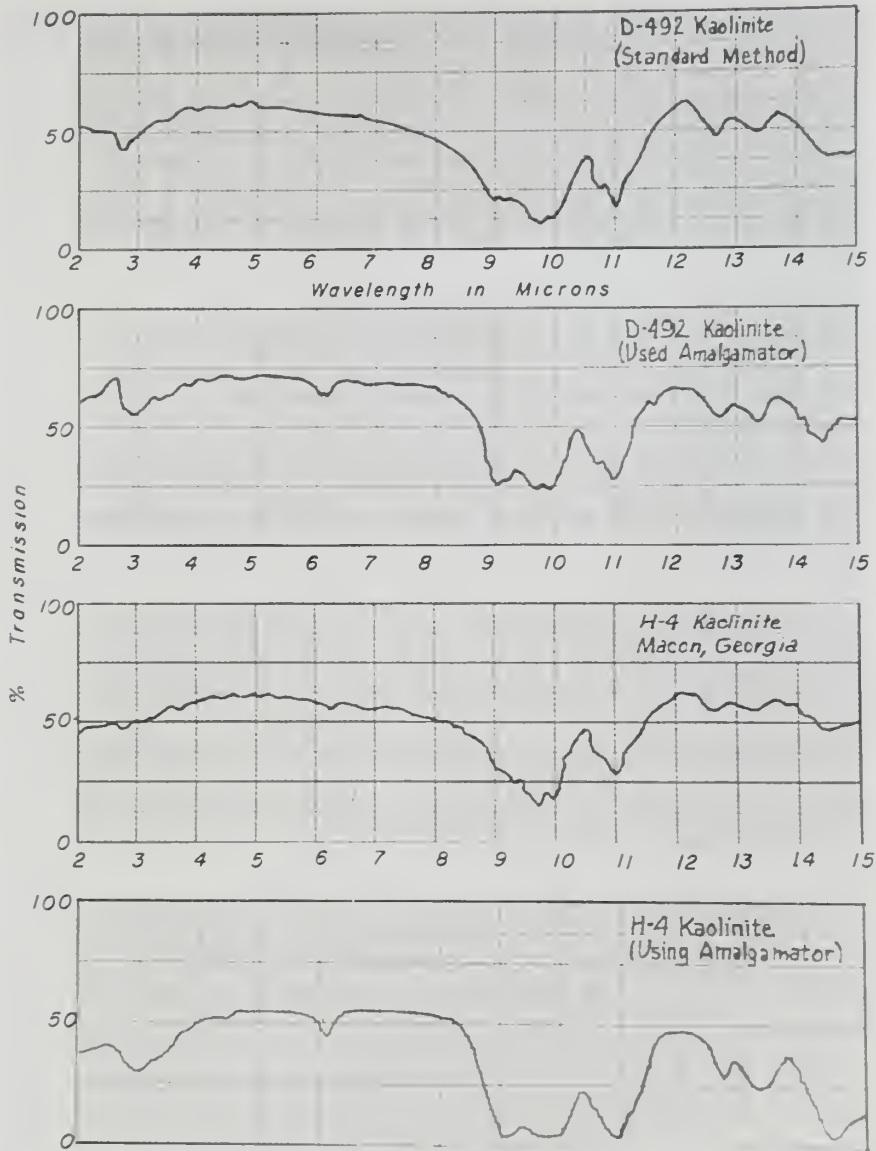


Figure XXI. Kaolinite Spectra Showing Amalgamator Effects.



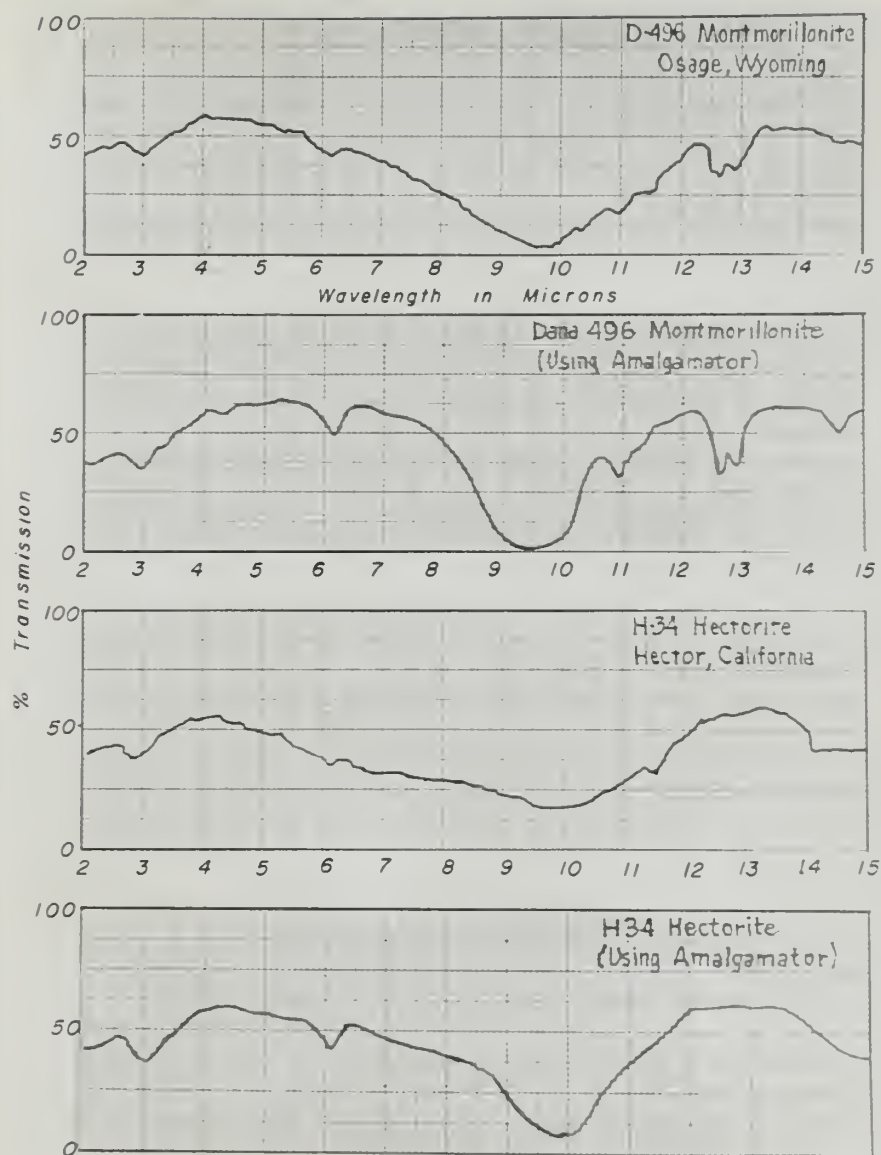


Figure XXII. Montmorillonite and Hectorite Spectra Amalgamator Effects.



to scattering effects described by Keller<sup>20</sup> and Kirkland<sup>28</sup>. Since the use of the amalgamator reduces the particles to an estimated size below three microns with the peaks being more clearly defined, the probability of the gradual transition in the standard method spectra being due to scattering is strongly reinforced.

#### D. 1:1 and 2:1 Lattice Spectra

During the initial phases of this investigation the hope was entertained that it would be possible by means of infrared analysis alone to quickly and accurately determine the identity of clay minerals in a given clay sample. As the investigation progressed it became evident that under the methods used, no characteristic differences existed between the spectra of the montmorillonites and illites. For example, the variations between the spectra of H-25, bentonite, shown in Figure XVI 4 and the H-35 and H-36 illites shown in Figure XX 1, 3 are insufficient to positively identify the clay minerals in question. Similar results occur in comparing the amalgamated mixture spectra of H-36, illite, shown in Figure XX 4 and D-496, montmorillonite, shown in Figure XXIII 4. Because of the widely different characteristics of these clay minerals and their affect on natural soils it is extremely important that the presence of the minerals be readily detected. It is therefore apparent that additional identification procedures are required to augment the results of infrared analysis in differentiating between the illites and montmorillonites.

In Figure XXIII typical spectra of kaolinite and montmorillonite are compared. It is readily apparent that a distinct difference between the two spectra exists. In all of the kaolinite spectra, an absorption band of strong intensity exists between 9 and 10 microns. An-







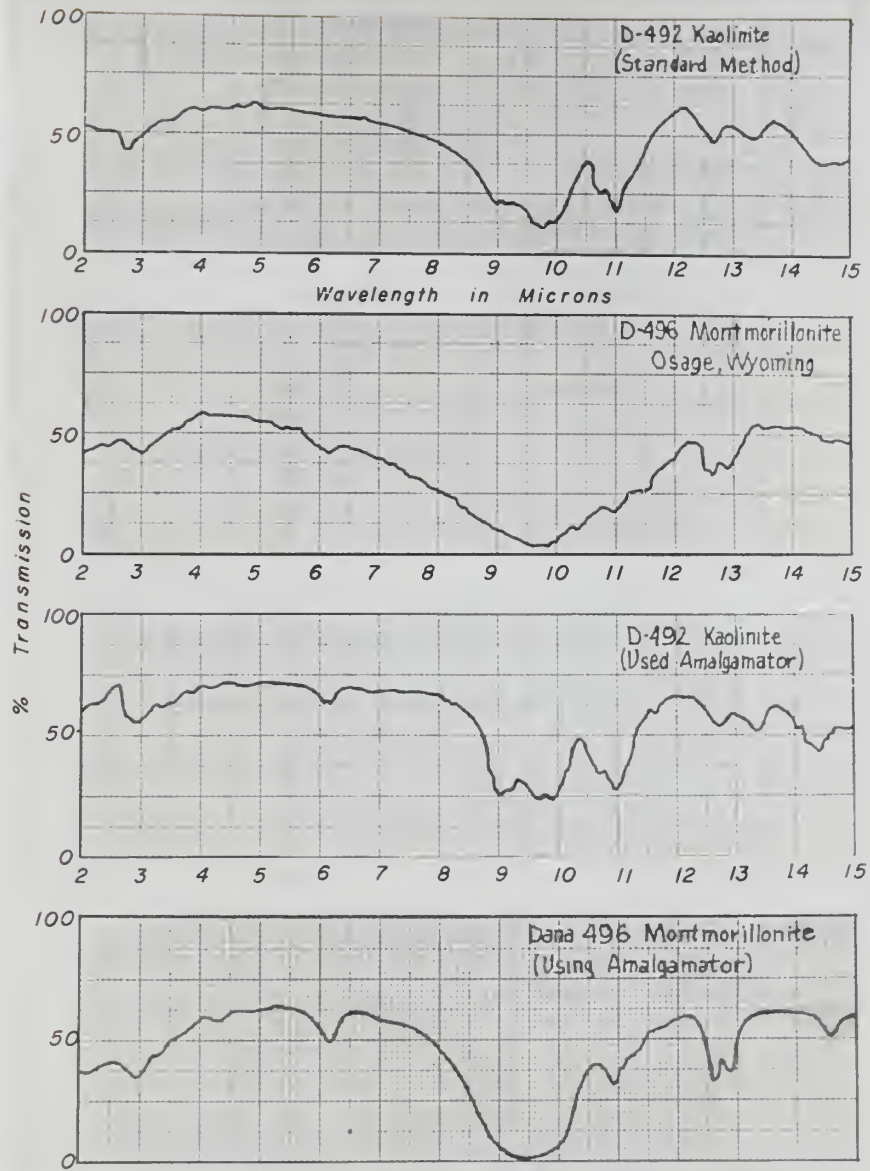


Figure XXIII. Comparing 1:1 and 2:1 Lattice Structure Spectra



other sharp band occurs at 11 microns, with absorption between 10 and 11 microns decreasing appreciable.

In the spectra of the montmorillonites the absorption decreases more or less uniformly from 10 to 12 microns. On the basis of all spectra run it is apparent that the presence of the clay mineral kaolinite can be accurately determined by means of the sharp drop in absorbance which occurs between 10 and 11 microns.

The most obvious reason for the difference in the spectra of montmorillonite and kaolinite lies in the basic difference in the crystal lattice structure of the two minerals. The lattice structures are discussed in Part II D. It would appear to be a natural conclusion that the differences in the 1:1 lattice of the kaolinites and the 2:1 lattice of the montmorillonites would be reflected in the spectra of the two minerals. It would further be quite probable that much less difference in the spectra would be expected in the case of montmorillonites and illites which both possess 2:1 lattice structures.

The spectra of silicic acid and alumina were run to determine if these compounds which are similar chemically to the major constituents of the clay minerals would produce spectra which could be related to those of the clay minerals. These spectra are shown in Figure XXIV. The curve of silicic acid ( $\text{SiO}_2 \cdot \text{H}_2\text{O}$ ) resembles superficially that of the montmorillonites. In view of the presence of two silica sheets to one of alumina in the 2:1 lattice minerals this resemblance could be expected.

It was theorized on considering the relative increase in the percentage of alumina in the 1:1 lattice structures as compared to the 2:1 lattice structure, that the differences in the spectra of the kaol-



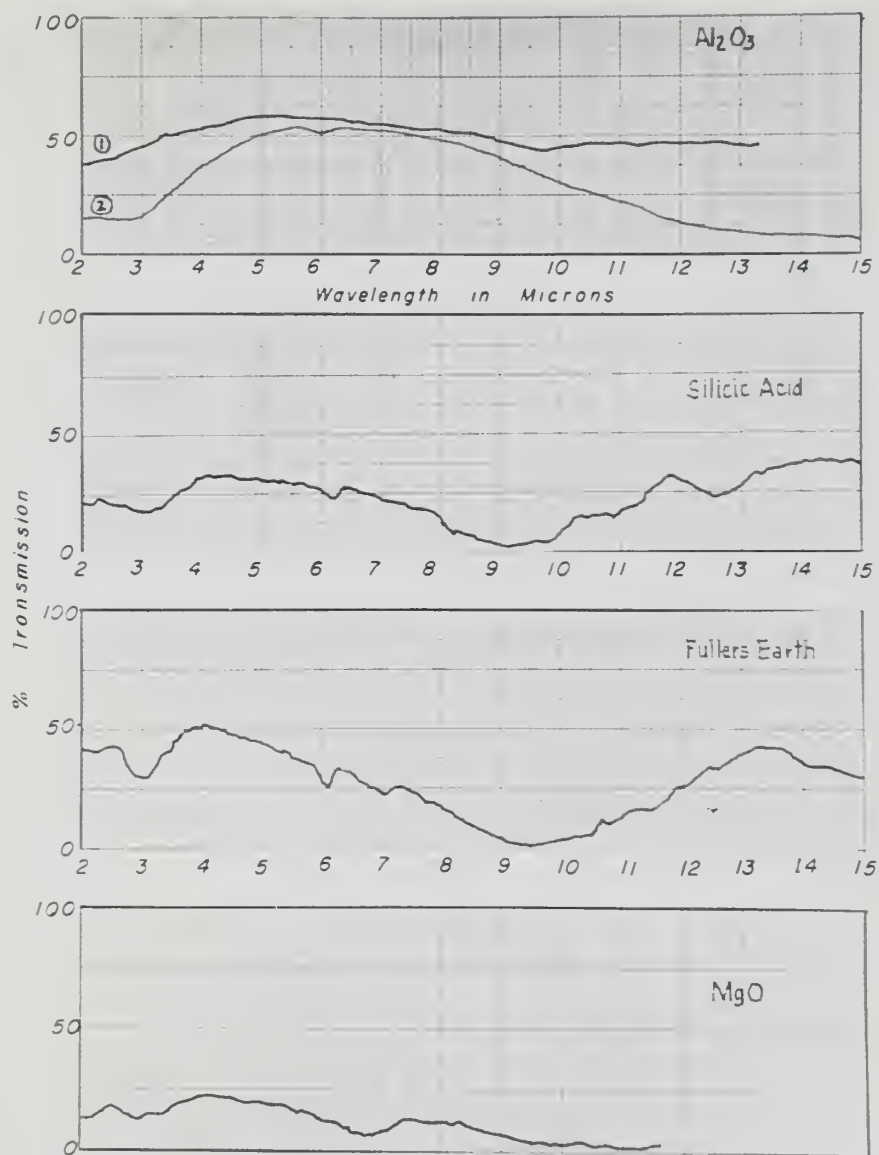


Figure XXIV. Spectra of Alumina, Silica, and Magnesium Compounds.



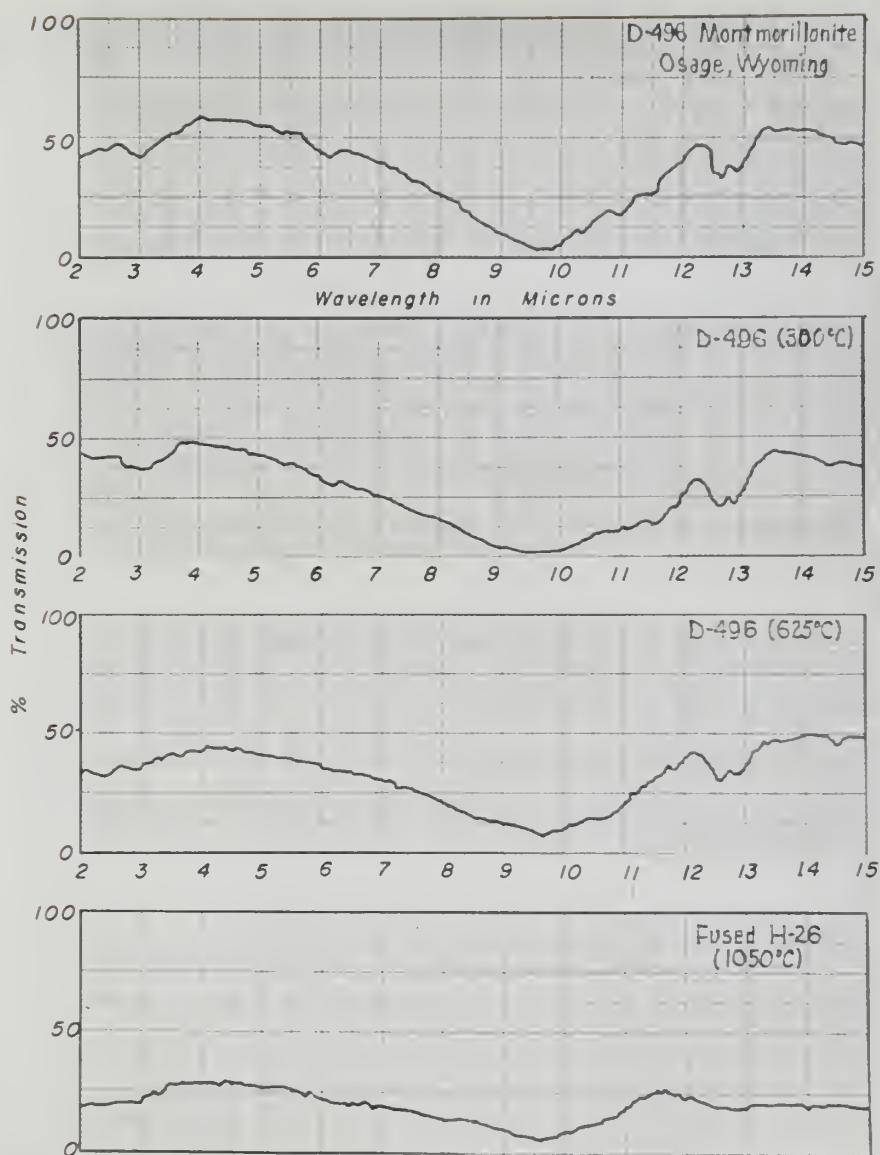


Figure XXV. Effect of High Temperature on Clay Mineral Spectra





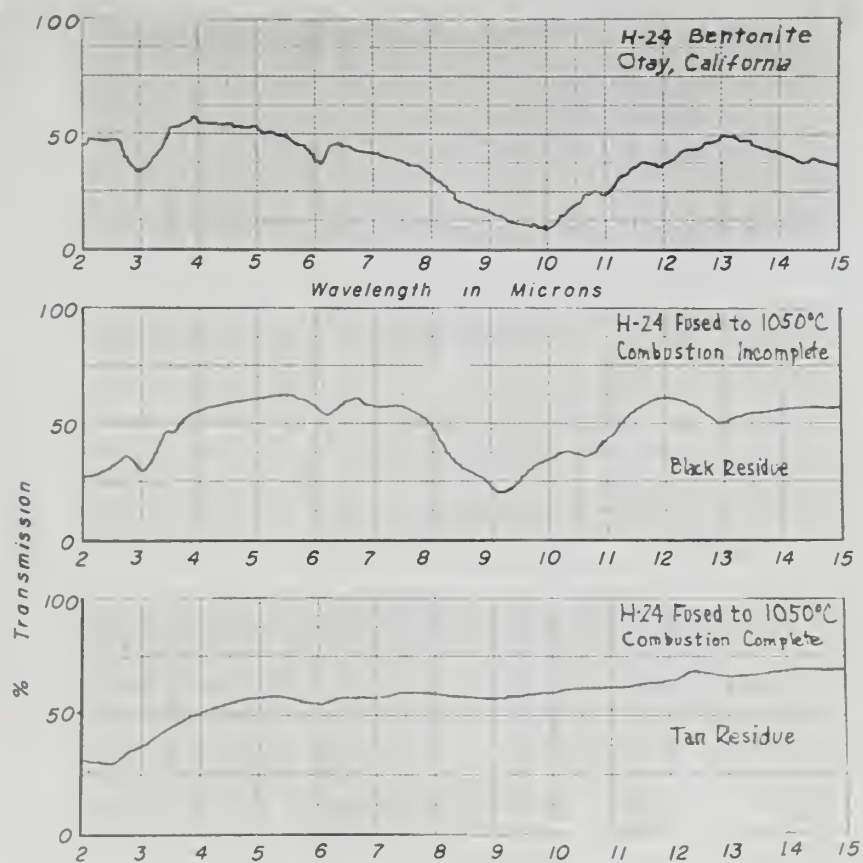


Figure XXVI. Effect of Incomplete Combustion on Spectra.



inites and montmorillonites (or 1:1 lattice and 2:1 lattice) could be related to the increase of alumina. On this basis it was felt that the spectrum of alumina ( $\text{Al}_2\text{O}_3$ ) would produce an absorption band at 11 microns, to correspond with the band that appears at 11 microns in the kaolinite spectrum. Such a theory was not confirmed by the results shown in Figure XXIV 1.

#### E. Effects of Temperature

The application of high temperature to clay minerals and the resulting effect of this temperature on the spectra of clay minerals was investigated. The results are shown in Figures XXV and XXVI. Samples were heated in a high temperature oven to temperatures which just exceeded those at which definite endothermic or exothermic reactions were observed in differential thermal analysis of the clay minerals.

Curve 1 of Figure XXV shows the spectrum of the montmorillonite prior to heating. In curve 2 a small decrease in the free OH band at 3 microns and the adsorbed water band at 6.2 microns is noted. Since most of the free water was removed in the clay prior to producing curve 1 by oven drying at 105° Centigrade, the dehydration of the clay at 300° Centigrade is only slightly increased.

In curve 3 the bonded and free OH stretching bands at 2.5 - 3.0 microns and the band at 6.1 microns all related to absorbed and lattice water have been eliminated. This result corresponds to the generally accepted theory that the second endothermic peak is the result of a phase change caused by the lattice and adsorbed water all being driven off. At 1050° Centigrade the clay loses its crystalline structure and a characteristic exothermic peak is observed in the differential thermal curve. The



resulting spectrum for this phase change is shown in curve 4 of Figure XXV and again in curve 3 of Figure XXVI.

The results of infrared analysis on the fused residue of H-24 bentonite, is shown in Figure XXVI. In running differential thermal curves on H-24 which had been saturated with piperidine, an organic compound, R. A. LITKE found that identical samples run under the same apparent conditions, but in different furnaces, produced residue which was completely different in appearance. The DTA curves also varied appreciably. LT LITKE concluded that the change was the result of incomplete oxidation (and combustion) of the piperidine caused by a partially restricted flow of air in one of the furnaces.

At his request, infrared analysis was performed on the residue of the two differential thermal runs. The results substantiated his conclusions. In curve 2 the presence of carbon from the partially ignited piperidine is confirmed by the presence of the C-H stretching band at 3.4-3.6 microns and the C-H bending band at 6.8-7.5 microns. The presence of water in the residue as shown by the peaks at 3 and 6.2 microns is considered to be due to the absorption of moisture from the air by the residue which exhibited many of the qualities of activated charcoal in this respect and was not immediately placed in a desiccator.

In curve 3 the piperidine has been completely oxidized and no evidence of any organic residue is indicated.

Another important result is shown in Figure XXVI. Although both clays were heated to the same final temperature, only in the case of complete combustion was there an exothermic reaction indicating a loss of crystalline structure. The loss of structure is verified in





curve 3 by the featureless spectrum. No change of crystalline structure is indicated by curve 2 verifying the absence of the characteristic exothermic reaction in the DTA. The absence of the structural change in the incompletely oxidized sample is considered to be due to a shielding of the clay by the carbon deposits which thus prevented the phase change.

#### F. Effect of Organic Ions

The effect of certain organic compounds saturating clay minerals was investigated to determine how the infrared spectra would vary. Saturated clays were prepared by R.A. LITKE for his work in DTA. The resulting spectra are shown in Figures XXVII and XXVIII. In Figure XXVII, a montmorillonite was first saturated with HCl to produce a monoionic H-clay. As shown in curve 2, saturation with HCl has changed the spectrum indicating that the clay structure has been modified. The fact that over-saturation with HCl does modify a clay has been confirmed extensively in the literature.<sup>4, 10</sup>

In curves 3 and 4 a properly prepared H-clay was saturated with pyridine and in addition the clay of curve 4 was resaturated with H<sub>2</sub>O<sub>2</sub> to remove the pyridine. It is evident that the presence of the ion had no significant affect on the curves 3 or 4.

In Figure XXVIII two montmorillonites were saturated with piperidine. The presence of the piperidine is shown by a broadening of the band at 3-4.5 microns due to C-H stretching and an additional band at 6.8-7.5 microns attributed to C-H bending in curves 2 and 4; however, the general characteristics of the montmorillonite spectra remained unchanged.

In Figure XXIX powdered alpha-cellulose was mixed with montmorillonite in the percentages indicated in the figure. The resulting





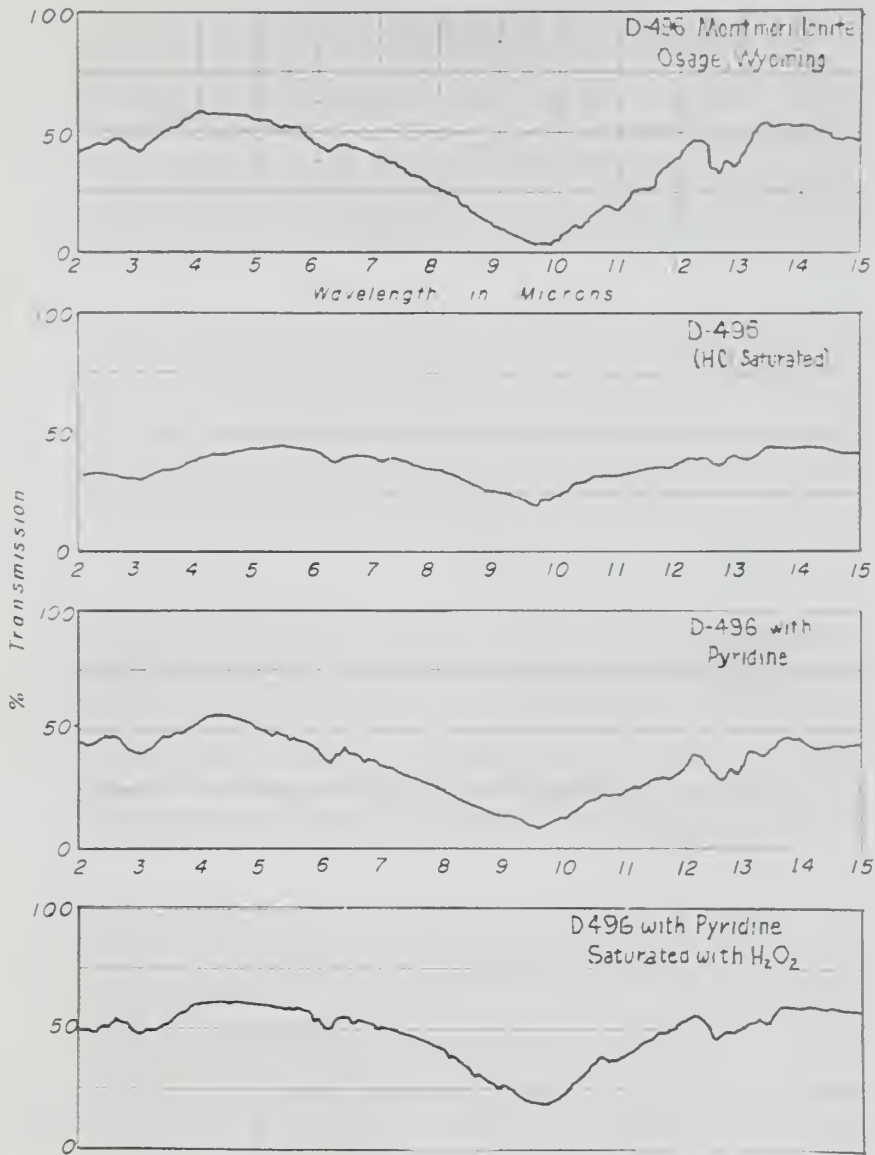


Figure XXVII. Effect of Ionic Saturation on Spectra.



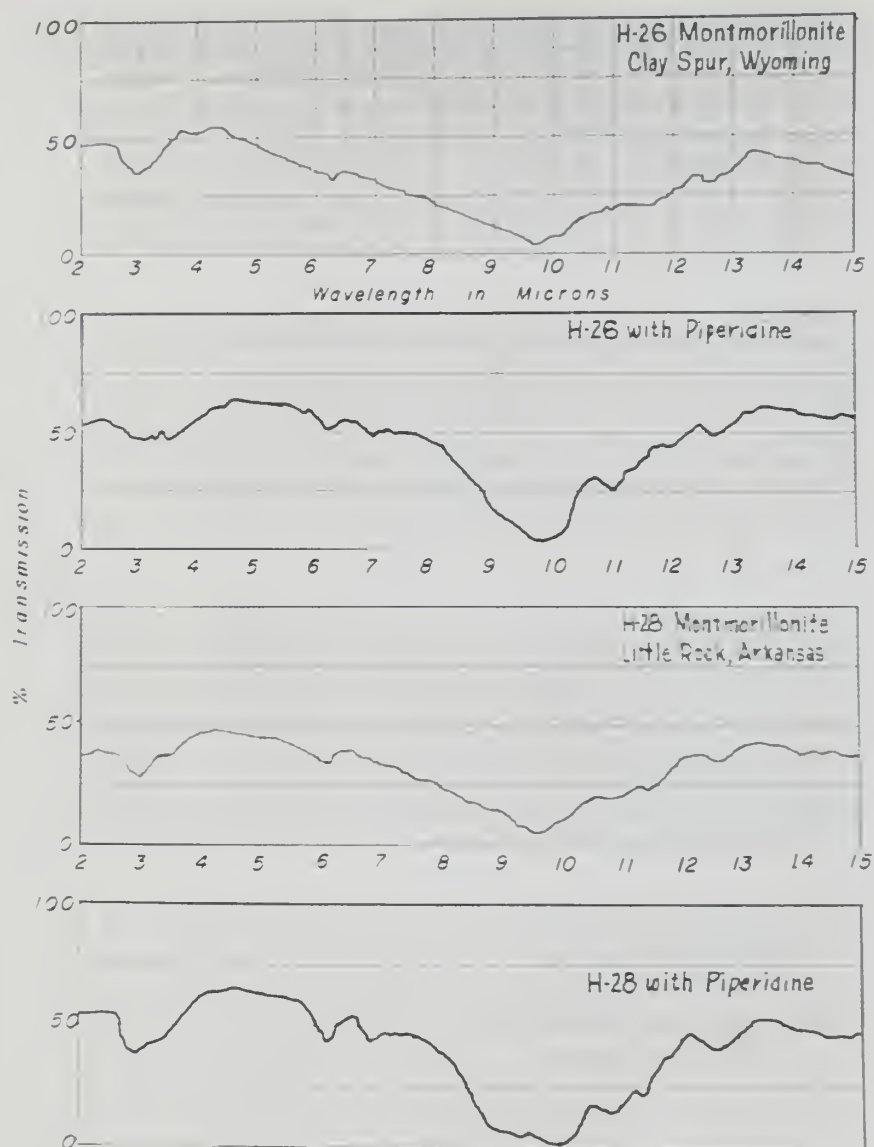


Figure XXVIII. Effect of Piperidine on Montmorillonite Spectra.



effect of alpha-cellulose on the spectra is shown in curves 2 and 3 with curve 4 being included for reference. The most apparent change in spectra is a marked increase in the intensity of the C-H stretching band at 3 microns. The alpha-cellulose even in relatively high percentages did not have as much effect on the montmorillonite curve as was anticipated.

#### G. Effect of Inorganic Ions

Spectra were run on H-35, illite, and D-492, kaolinite, which had been saturated for a previous investigation to produce H, Ca, K, and Mg clays. In all cases the results were inconclusive. The resulting curves differed only insignificantly, with the variations possibly due as much to machine "noise" as to the presence of the inorganic ions. The clays were prepared several years ago and stored under varying conditions indicating a possibility that the clays could have different composition than when originally prepared. In view of the similarity of the curves and the difficulty of showing any variation whatsoever by the reproduction method used for spectra the actual curves are not included. Available time did not permit the preparation of fresh samples to augment this phase of the investigation.

#### H. Mixed Clay Minerals

D-492, kaolinite, and D-496, montmorillonite were combined in the proportions indicated in Figures XXX and XXXI. In Figure XXX the montmorillonite reduces the intensity of the distinctive kaolinite transmission peak at 10.5 microns. In Figure XXXI the large percentage of montmorillonite nearly obscures the characteristic kaolinite spectrum. Using proper standards and quantitative techniques the possibility of



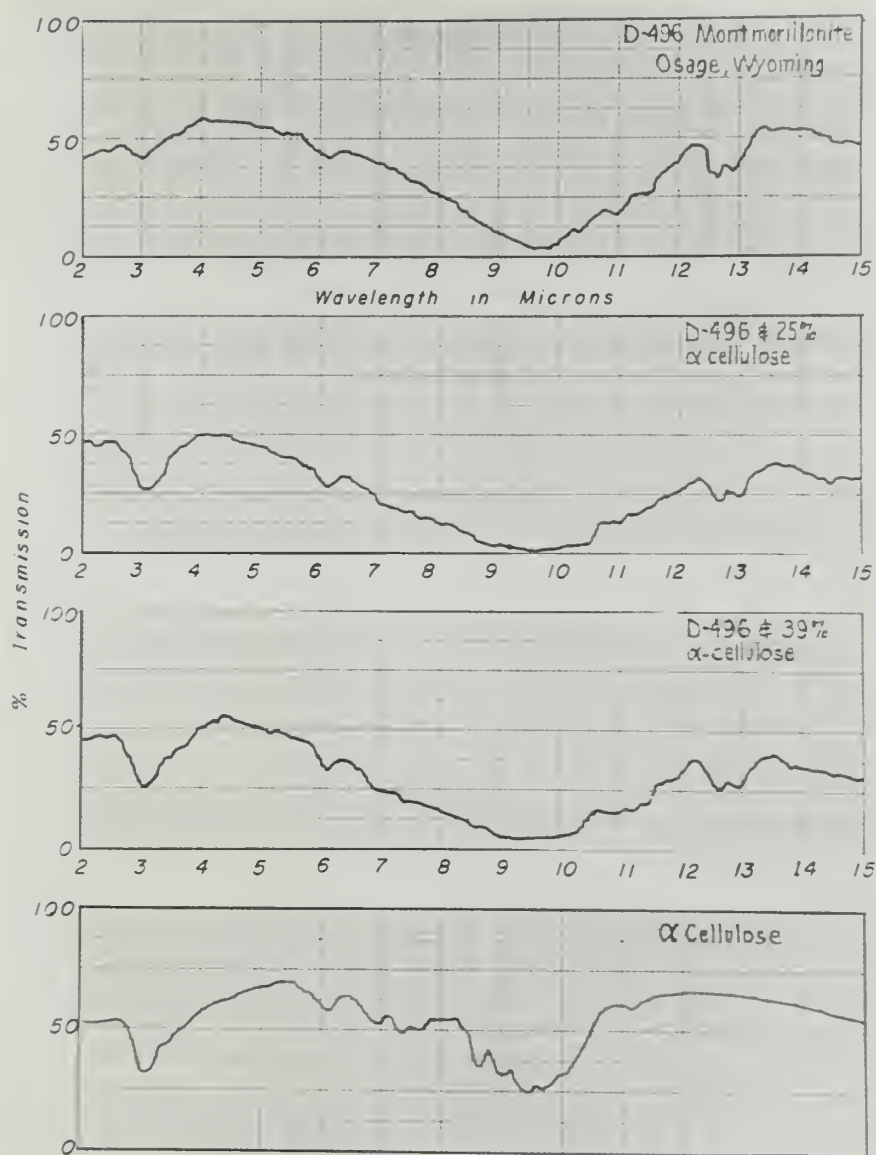


Figure XXIX. Effect of alpha-cellulose on spectra.





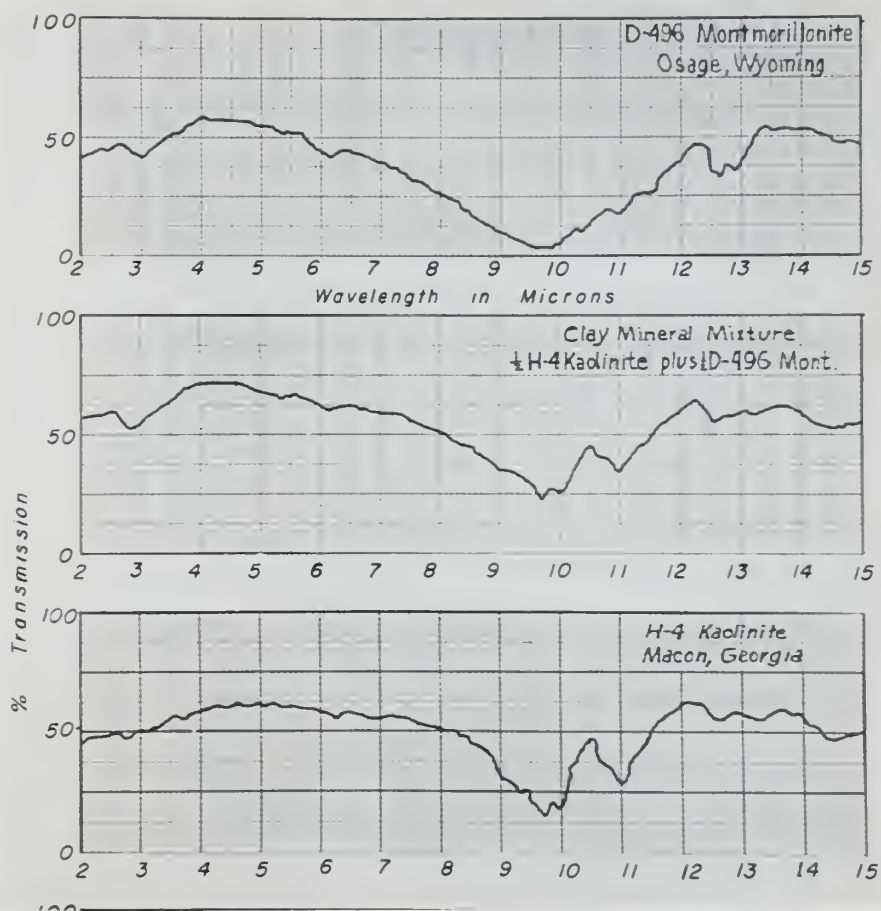


Figure XXX. Mixed Clay Mineral Spectrum



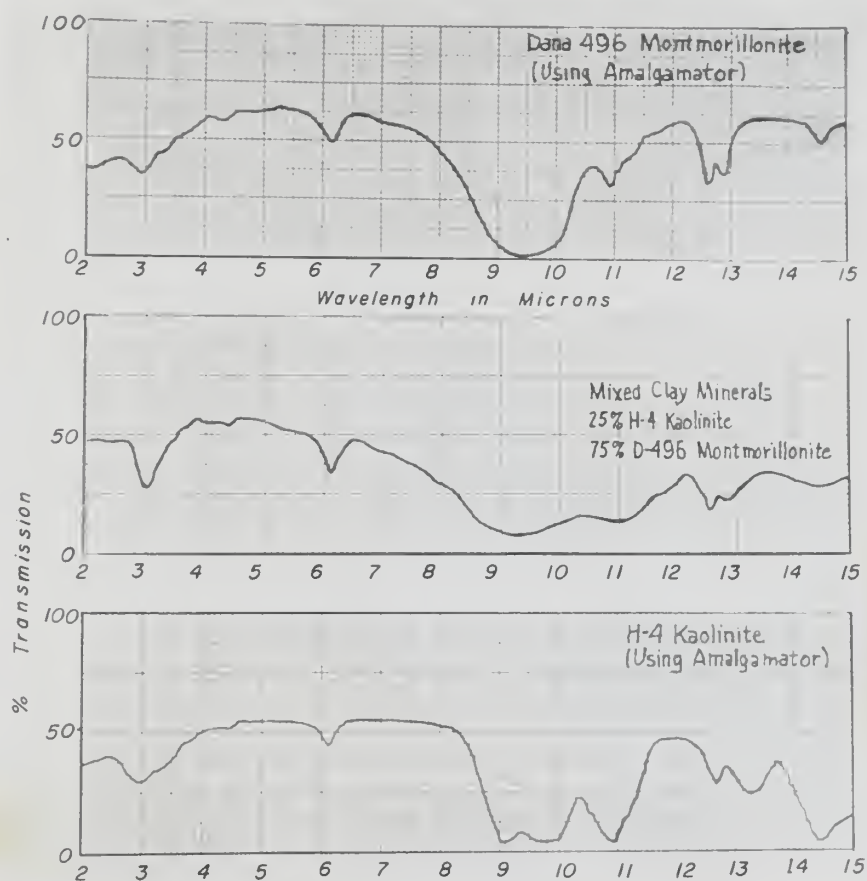


Figure XXXI. Mixed Clay Mineral Spectrum



reasonably accurate quantitative analysis by infrared is indicated.

### I. Natural Clays

Infrared spectra were run on three clay samples received through the state Testing Laboratory in Latham, New York. Samples were received in moisture sealed test cylinders and could be classed as moderately disturbed samples. The resulting spectra are shown in Figure XXXII.

Curves 1 and 2 are from natural clays from two locations along the St. Lawrence Seaway. The samples were both a greenish-gray in color and appeared to be reasonably homogeneous and free of varves. These samples were run at their natural moisture content as received. The spectra were very close in appearance and could therefore be reasonably assumed to be of the same composition. On the basis of the spectra these clays were considered to include illite and hectorite clay minerals. The hectorite was assumed on the basis of the spectra for this mineral produced by Bray and Stevens<sup>1</sup> which showed a distinct band at 7 microns. Previous DTA and X-ray analysis of these clays in 1955 graduate work have indicated a possibility of both illite and hectorite in the clay.

In curve 3 the clay sample was from the Phoenicia Stony Clove (NY) bridge site. This clay appeared to possess some silt content, was reddish in color and was structurally weak when dried. A small portion of the sample was tested for swelling characteristics in a beaker of distilled water. The presence of montmorillonite was indicated by the results of this test. A typically montmorillonite type spectra resulted.

The presence of quartz was verified by the typical quartz doublet at 12.5-13 microns in all three clays.



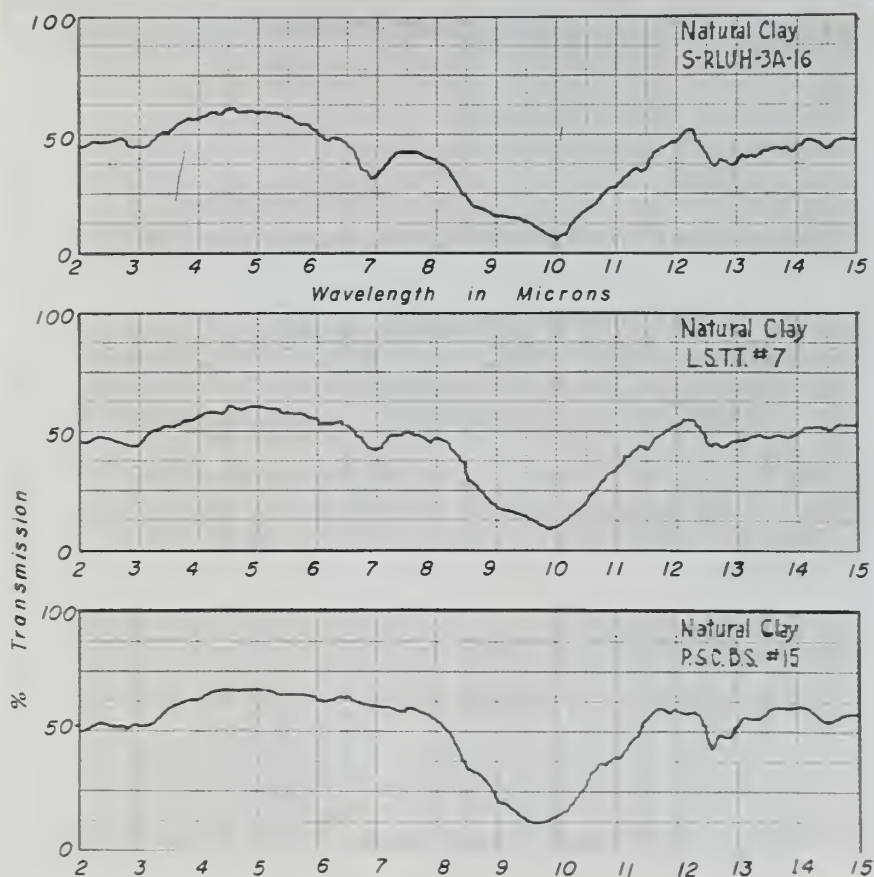


Figure XXXII. Natural Clay Spectra





## PART V

## CONCLUSIONS

Following careful consideration of the results of this investigation and considering the information available in the literature, the conclusions listed numerically below were obtained. Attention is invited to the fact that this research is preliminary in nature only, since the time available for its accomplishment precludes the possibility of it being anything else. The conclusions resulting below should consequently be considered in this light and used with judgment.

(1) Infrared analysis can be successfully applied to the field of clay mineralogy and the results gained from the technique are of considerable value in clay mineral identification.

(2) The potassium bromide technique for preparation of sample and reference windows is completely satisfactory for clay mineral analysis.

(3) Infrared spectra of greater accuracy and clarity can be produced from samples mixed with a dental amalgamator than those mixed by hand.

(4) Infrared spectra of sufficient accuracy for rough survey work of a qualitative nature can be produced by the standard mixing method described in Part III C, Procedures.

(5) Satisfactory spectra can be produced with windows that are cracked or broken providing sufficient window exists to cover the slit opening of the spectrophotometer.

(6) Optimum results were obtained using 2-3 milligrams of clay mineral sample when mixed by the standard method and 0.8 milligrams of sample when mixed with a dental amalgamator.



(7) A pressure of 15,000 pounds for ten minutes or a pressure of 20,000 pounds for five minutes on the window die produces equally satisfactory windows. The limitations of the available equipment or time requirements are the only factors which should require consideration in choosing which of the above combinations would be the most satisfactory.

(8) The spectra of clay minerals exposed to high temperature are modified in a manner which confirms the generally accepted theories of differential thermal analysis.

(9) The presence of kaolinite of 1:1 lattice structure clay minerals can be readily detected by infrared analysis.

(10) The presence of 2:1 lattice structure clay mineral can be readily detected by infrared analysis; however, no method of differentiating between montmorillonite and illite types of 2:1 lattice structure minerals was found.

(11) The presence of organic ions on a clay mineral can be detected providing a sufficiently large concentration of the organic ion has been taken up by the clay.

(12) The presence of even a relatively large concentration of organic material in a clay does not affect the spectra enough to prevent identification of the clay mineral. This is also true for clays saturated with organic ions.

(13) Infrared analysis is considered to be adaptable to quantitative analysis of clay minerals with modification of techniques and establishment of suitable standards.

(14) Infrared analyses can be performed more rapidly than other



recognized identification techniques. A much smaller quantity of sample is required and windows may be saved for future reference and reruns.

(15) Infrared analysis is an important and valuable addition to clay mineral investigations; however, as in all other techniques, it is limited in its capabilities in certain cases and the information it gives must be augmented by data from other sources.



## PART VI

## RECOMMENDATIONS

A. Use of Amalgamator

The writer recommends that further study in this field be performed using an amalgamator for all sample and KBr mixing. The amalgamator will appreciably reduce the amount of time necessary for grinding clay samples and give a mixture of greater uniformity. At the same time a much finer clay particle size results than that produced by hand grinding.

B. Accurate Sample Weights

In most of the sample quantities discussed, a range of weights was given rather than a specific value of weight. This was necessary because of the difficulty of accurately weighing extremely small quantities by means of the available analytical balance. For further study, the procurement and use of a suitable micro-balance is strongly recommended. Such a balance would be particularly necessary in quantitative work.

C. KBr Window Die

The window die fabricated for this research is not considered to be completely satisfactory. The rectangular construction of the die opening makes it difficult to remove the windows without cracking or breaking them. Although successful spectra can be produced with such windows in some instances, an alternative die producing a circular disk window thus removing points of stress concentration is advocated.

A die can be made from three rectangular blocks of tool steel such as Atlas "A" steel produced by the Allegheny Ludlum Steel Corporation







and either a  $5/8$  inch diameter high speed carbon steel drill or a  $5/8$  inch diameter rod 2  $1/2$  inches long of tool steel. Suggested dimensions of the three blocks are 2 x 2 x 1 inches for the single base piece and 1 x 1 x 2 inches for the two top pieces. Two holes should be drilled on 1  $3/8$  inch centers in the two top pieces with the holes in one top block being tapped for  $1/4$  x 20 threaded bolts and those in the other top block being drilled to a  $9/32$  or  $5/16$  inch diameter to clear the  $1/4$  inch bolts in a manner similar to the die shown in Figure X.

The top blocks should then be bolted together and placed over the base block with the whole assembly placed in a heavy duty drill press. A  $5/8$  inch hole is drilled through the top and bottom pieces in the center of the 2 x 2 inch area. If a drill is used as the  $5/8$  inch bearing block and plunger the drill shank is cut into two 1  $1/8$  inch lengths by a suitable cutting wheel. If a  $5/8$  tool steel rod is used it should be cut into similar lengths and then hardened along with the other pieces of the die. The drill rod would not require additional hardening. The tool steel should be hardened to a Rockwell C hardness of 60-65. After hardening, the upper surface of the bearing block and the lower surface of the plunger should be polished in a surface grinder to give a disk window of uniform thickness.

Construction of such a die requires no special machining techniques and will produce a  $5/8$  inch diameter window. Twice the amount of sample and KBr would be required to produce a window of similar thickness to those made in the rectangular die. To give the desired transparency to the window, a hydraulic jack capable of exerting 31,000 pounds on the die for ten minutes or 41,000 pounds for five minutes would be required.



Hardened steel plates above and below the die would be required to prevent distortion of the faces of the press as pressure is applied.

Construction of this die would permit easy removal of sample windows and would virtually eliminate breakage caused by removing windows from the die.

For quantitative analysis the procurement of an evacuated die such as the Hilger Die marketed by the Jarrell Ash Company, 26 Farwell Street, Newtonville, Massachusetts, should be investigated. This die produces a disk  $1/2$  inch in diameter which has improved strength uniformity, and transparency because of the evacuation of air from the chamber as the window is being pressed. Air thus cannot be trapped in the disk to cause variation in the absorption characteristics. Such a die is not deemed a necessity for purely qualitative work.



## PART VII

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